USING THE RIETVELD METHOD FOR THE ESTIMATION AND CHARACTERIZATION OF CRYSTALLINE AND AMORPHOUS MATERIAL IN THE CLAY FRACTION OF TEN HAWAIIAN SOILS

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ABSTRACT

The ability to measure the amount and composition of amorphous material in the clay fraction of soils offers opportunities for discovering the roles that these materials play in influencing soil behavior and performance. An objective of this research was to developed a methodology for the determination of the crystalline phase concentrations and the total amorphous material by the Rietveld method for ten agriculturally important Hawaiian soils. The oxide composition of the amorphous material was estimated by difference after the assignment of oxides found by X-ray fluorescence were allocated to the crystalline phases. A large disparity was found between the total amorphous material determined by the Rietveld method and the amorphous material determined by oxalate extraction, possibly because the two methods are reporting different portions of the clay fraction. For the first time correct crystalline phase concentrations can be determined because reliable estimates of the total amorphous material can be made.

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INTRODUCTION

In their 1973 paper Jones and Uehara showed that a substantial amount of gel-like material coats the solid particles in Hawaiian soils. Later it was found that most of the gel coatings seen in transmission electron micrographs could be removed by chemical extractants including, in some cases, H_2O_2. Because the gel coating could be removed by one or more chemical extracting agents, the conclusion was drawn that the gel coatings constituted a major portion of the noncrystalline fraction of the soils.

Two questions about the gels have remained unanswered until the present. First, the chemical composition of the gels was unclear because depending upon the method of extraction, different conclusions could be drawn. Secondly, and perhaps most importantly, was the dubious conclusion that chemical extractants were removing all of the noncrystalline materials. In some cases the extractants might remove a portion of the crystalline phases in addition to the noncrystalline material. In most cases the solid particles seen in electron micrographs appeared "clean" after chemical extraction; however, these particles may in themselves be noncrystalline. Until recently the only conclusion that could be drawn was that we could not estimate the actual weight fraction of the amorphous components, and we could not determine the true chemical composition of the noncrystalline fraction of highly weathered Hawaiian soils.

The development of the Rietveld method of quantitative analysis has provided a tool for reliable estimates of crystalline and amorphous phases in powder samples. By this method a calculated full-pattern is fit to the observed XRD pattern. Because the Rietveld method includes the full-pattern, instrumental permutations as a function of 2θ are largely compensated. Originally the Rietveld method was employed for the refinement of crystalline structures. Later the structures of the most common phases were cataloged in the form of $hk\ell$ files which enabled their routine usage by bypassing the need for further structure refinement except in special cases. Each phase represented in an XRD pattern is assigned a Rietveld scale factor. The sum of the crystalline phases is then normalized to 100%. Because crystalline phases do not include the amorphous fraction, their percentages are reported higher than their true values. Therefore, with an added internal standard (spike), the abnormally high value enables a reliable estimate of the sample's total amorphous content. By knowing the composition of each crystalline phase and having the results of a total chemical analysis, the remainder of the oxides that are not assigned to the crystalline phases are assigned to the amorphous fraction.

Mineralogical and amorphous percentages of the clay fraction of ten Hawaiian soils were acquired with the SIROQUANT© program (a Rietveld method of analysis). Ten agriculturally important Hawaiian soils chosen for this study were collected by J. Jackman (1994). The main objective of Jackman's 1994 thesis was the prediction of P sorption capacity of soils based on quantitative XRD analysis of the crystalline portion of soils. The current investigation is intended to add to his mineralogical investigation by using the same soils with new analytical techniques that focus on the amorphous content of the soils.

DISCLAIMER

The use of the trade name SIROQUANT© does not act as an endorsement of this product.

OBJECTIVE

The objectives of this study are to 1) estimate the total amorphous fraction of ten agriculturally important Hawaiian soils by the Rietveld method, 2) estimate the oxide composition of the amorphous fraction of the soils, and 3) quantify the crystalline composition of the soils.

LITERATURE REVIEW

Since the publishing of "A Profile Refinement Method for Nuclear and Magnetic Structures" (Rietveld, 1969) there has been a number of profile, or whole-pattern, refinement computer programs written that utilize mathematical devolution of diffraction peaks to solve crystallographic structures (Weiss et al., 1983; Wiles and Young, 1981; Will et al., 1983).

Young and Prince (1982) define the Rietveld method as "whole-pattern-fitting of calculated to observed powder patterns through least-squares refinement of model(s) for the structure(s), diffraction optics effects, and instrumental factors. A key feature is the feedback, during refinement, between improving knowledge of the structure and improving allocation of observed intensity to individual Bragg reflections."

Today personal computers are capable of performing complex calculations very quickly, making Rietveld analysis a tool available to many researchers (Jenkins, 1994). Presently there are several Rietveld programs written for X-ray diffraction data on the market that can be used with fast personal computers. One such Rietveld program named SIROQUANT© was written for the Division of Coal and Energy Technology, CSIRO in Australia (Taylor, 1989). Details of the SIROQUANT© program were published by Taylor (1991) and have since been updated to include a Windows version.

The SIROQUANT© program is marketed by SIETRONICS Pty., Ltd. Lucas Heights Research Laboratories, Menai, New South Wales 2234, Australia.

The program can be used to determine the crystal structure of minerals and to estimate the percentage of minerals present in a sample. Prior to the use of the Rietveld method, mineral percentages were estimated by either guessing at the integrated intensities of specific mineral peaks or by a comparison to a known spike weight percent added to the sample (Klug and Alexander, 1974). For example, using method 1, the percentage of quartz in a sample was estimated by integrating the intensity of the 101 peak in comparison to all other quartz peaks present. This method generally caused over estimation of quartz because of the relatively high 101 peak caused by preferred orientation. At best, method 1 could only report amounts as abundant, moderate, small, or trace. Using method 2, the comparison of peak height to a known-weight percentage could only be accurate if both peaks were well resolved (no overlap) and preferred orientation was absent. Method 2 also ignores possible mixing and weighing errors associated with the addition of an internal standard, which may not be a valid assumption.

AB INITIO ANALYSIS

Ab initio implies that by starting with the same default parameters, refinement calculations will produce the same results each time. Prior to the advent of fast personal computers assumptions (sometime erroneous) had to be made because most computers could not preform the many iterations needed to do *ab initio* analysis. Todays personal computers have large memory capacity and high speed capabilities which enable *ab initio* to be possible. The SIROQUANT© program provides *ab initio* analysis of multi-phase mixtures (all calculations are performed on each new analysis with no assumptions made for any parameters) that to date gives the most accurate assessment of crystal structure and mineral percentages. These types of analyses were not readily available to investigators less than ten years ago.

X-RAY SOURCE AND PARTICLE SIZE

Bish and Post (1993) showed that the quantitative analysis of Al_2O_3-Fe_2O_3 mixtures was inaccurate using Cu$K\alpha$ radiation, but much more accurate by the use of Fe$K\alpha$ radiation because of reduced absorption effects.

Diffraction intensity variations due to absorption effects of differing particle sizes can be partially corrected by the Brindley model (Brindley, 1945). Brindley's model addresses multi-domain (multi-crystallite) particles with a domain size significantly smaller than the particle size. Brindley referred to the absorption of X-rays by various size particles as "microabsorption." The microabsorption effect predominates when large particles with small domains have highly contrasting absorptivities between the diffracting particle and the matrix. Brindley proposed a factor to take into account the mass absorption coefficient of each phase. His equation is as follows:

$$\tau_a = \frac{1}{V_a} \int_0^{V_a} \exp^{-(\mu_a - \bar{\mu})x} \, dV_a \, , \tag{1}$$

where V_a is the volume of a particle (or crystal) of substance *a*, μ_a is its linear absorption coefficient, $\bar{\mu}$ is the mean linear absorption coefficients of powder matrix, x is the path of the radiation in the particle of *a* when reflected by the volume element dV_a, and τ_a is the particle absorption factor.

Taylor and Matulis (1991) utilized the Brindley model in the SIROQUANT© program to correct particle microabsorption effects which are dependent upon the mean mass absorption and particle diameter (path length) of each phase. The mass absorption coefficients for each phase are incorporated into the program. It is only necessary to enter particle size estimates in order to perform a "Brindley Correction."

SIROQUANT© is one of the few programs that incorporates this factor into the calculation for quantitative analysis.

Cullity (1978) defines all real crystals as being imperfect, in the sense that they have a mosaic structure. He suggests that extinction is absent in an ideally imperfect crystal and in order to ensure or reduce extinction, powder specimens should be ground as finely as possible. Grinding tends to decrease the crystal size by disorienting the mosaic blocks and straining them ununiformly.

Because the SIROQUANT© program does not account for extinction effects, the soil sample size chosen for this work was <2 μm in diameter as determined by centrifugation utilizing Stokes law. One of the reasons standard reference material (SRM) corundum 674 was chosen as the internal standard (spike) was because it is certified as having a <2 μm diameter particle size.

INSTRUMENTAL CONFIGURATION

Rietveld analysis utilizes the entire X-ray diffraction pattern, thereby reducing the systematic effects of instrumental configuration. Instrumental configuration generally includes: 1) instrument zero angle, 2) monochrometer 2Θ angle, 3) tube anode and 4) radiation type (laboratory X-rays, neutrons or synchrotron).

Bish and Chipera (1995) demonstrated the effect of sample displacement on unit-cell parameters refinement with and without a zero 2θ correction. By using a well characterized sample of SRM silicon 640b, they plotted the changes in unit-cell *a* parameters by artificially inducing specimen-displacement, demonstrating the need to perform zero 2θ refinement. Bish and Chipera also mention that the importance of a well aligned diffractometer is evident by examining SRM unit cell parameters of published Rietveld refinements when zero 2θ refinement is utilized. Bish and Chipera also state that the wavelength of $CuK\alpha_1$ radiation is not universally agreed upon, and that a change in the 5th decimal place can account for a discrepancy of more than twice the estimated standard deviation of the certified SRM silicon 640b *a* unit-cell parameters.

When collecting data with a conventional X-ray source, Hill (1995) suggests that a monochrometer should be used to eliminate the $K\alpha$ doublet. By using single-wavelength data the reflection density is halved at no cost to the observation-to-parameters ratio, and single-wavelength data also eliminates systematic errors associated with analytical removal of the $K\alpha_2$ component of the $K\alpha$ doublet (Louër and Langford, 1988). Utilizing the SIROQUANT© program, the anode tube type, wavelength, and radiation type (laboratory X-rays, neutron or synchrotron) can easily be modified for each new sample analysis.

PREFERRED ORIENTATION

Crystals that display preferred orientation most commonly orient themselves on basal planes of tablets or on rod planes of needles, producing intensities greater than published values for these planes. Preferred orientation should be avoided when preparing a sample for X-ray diffraction because the increase in intensity can, if not accounted for, skew the percentages calculated by SIROQUANT© in favor of that mineral.

Bish and Reynolds (1989) discuss the problems associated with differing degrees of preferred orientation in quantitative analysis and stress that inaccuracies are exacerbated when using conventional reference intensity ratio methods that employ only one or two peaks.

The SIROQUANT© program allows the user to correct for preferred orientation of each specific mineral with the March-Dollase function. Dollase (1986) describes the application of the March model for Rietveld refinement to correct for preferred orientation. Dollase found that the March distribution displays the best overall performance of the available functions.

The function is as follows:

$$\text{Preferred Orientation } (P)_K = (r^2 \cos^2\alpha + \sin^2 \alpha / r)^{-3/2}, \qquad (2)$$

where α is the angle between the plane normal to the plane K (where K is used to denote the triplet (hkℓ)) and the orientation plane, and r is the refinable parameter (< 1 for plates and > 1 for rods).

Hill (1995) demonstrated the effect of applying the preferred orientation correction factor in the determination of Rietveld weight percentages for a mixture of known weight percentages. Hill's experiment shows that the March-Dollase function accurately compensates for preferred orientation in the mixture. Bish and Chipera (1995) state that besides differences encountered from sample to sample, there can also be variation within each sample due to orientation. Bish and Chipera found variations in reference intensity ratios (RIR) between six clinoptilolite samples due to preferred orientation. Because Rietveld analysis uses the full-patten, employing every data point of a digitized pattern, all peaks (not one or two) can be used to correct for preferred orientation (Hill, 1995).

FULL WIDTH AT HALF MAXIMUM (FWHM)

Rietveld (1969) simplified the formula for angular dependencies of the widths for diffraction peaks put forth by Caglioti et al. (1958) to:

$$\mathrm{FWHM}^2 = (U \tan^2 \theta + V \tan \theta + W), \tag{3}$$

where U, V, and W are the peak width parameters and θ is the Bragg angle. Prince (1995) pointed out that algorithms based on this form maybe unstable. The correlation among parameters can be high leading to refinement values becoming negative at some point in the pattern,which may cause the computer program to crash on an attempt to extract the square root of a negative number.

The SIROQUANT© program utilizes the formula as simplified by Rietveld (1969), emphasizing that *U*, *V* and *W* parameters should not be refined simultaneously. Taylor (1991) suggested that while refining the line widths, only *W* should be refined first (taking $W=(\text{FWHM})^2$) and then *U* and *V* are refined later if the data justifies it.

For X-ray diffraction data the crystallographic parameter *W* for peaks of single well-crystallized phases are generally narrower than peaks produced by minerals in soil samples which are due to atomic substitution within the crystal lattice, micro strain, and peak overlap (Taylor, 1991). Compared to conventional methods of mineral quantification, Rietveld analysis gives a more efficient treatment (devolution) of overlapping peaks (Hill, 1991). The SIROQUANT© program simplifies changing and reviewing the new values of *W* during refinement for each mineral phase. One drawback of the SIROQUANT© program is that only one *W* value can be used for all peaks of a given mineral. The average *W* works well for the estimation of mineral percentages; however, a unique *W* for each peak would give more information on peak width and position. Peak width is an indicator of crystallite size, and peak position indicates changes in the lattice parameters due to atomic substitution within the crystal lattice. Some have suggested that the ability to refine a *W* value specific for every peak of a given mineral should be incorporated into the next version of the SIROQUANT© program, although the extra calculations generated maybe very time consuming until more powerful personal computers are developed.

BACKGROUND

The SIROQUANT© program has the ability to fit the entire background to an analytical function instead of one or two measured peaks as in traditional integrated intensities methods. Baur and Fischer (1986) were successful in modeling the background of samples with high amounts of amorphous material by using a 5th order polynomial. Baur and Fischer's background function decreases exponentially from zero to approximately 10 degrees 2Θ, then produces three broad peaks at approximately 20, 45, and 80 degrees 2Θ. Von Dreele and Cline (1995) experimented with six different background functions for differing sample types. Richardson (1995) showed that by using Fourier-filtering, additional information within the background can be extrapolated. Richardson found that the background of an aluminophosphate sample showed broad peak positions close to those of the crystalline material. This evidence suggests that the amorphous component, although lacking long-range periodicity, has an atomic arrangement similar to that of the crystalline material.

The SIROQUANT© program can easily calculate and subtract the background as linear, quadratic, or a compilation of both for each new analysis. Background information can be easily extracted and used with other types of analyses (i.e. Fourier-filtering). The SIROQUANT© program can also subtract the background from the data pattern introduced by instrumental aberrations.

RESIDUALS

The SIROQUANT© program reports residuals for the observed and calculated patterns as Profile R factors and chi square (*CHISQ*) factors.

$$\mathit{Profile}\ R = \frac{\sum |Y_o - Y_c|}{\sum |Y_o|}, \qquad (4)$$

$$CHISQ = \left(\sum \frac{(Y_o - Y_c)^2}{Y_o\,(NO - NV)} \right)^{\frac{1}{2}}, \qquad (5)$$

where Y_o is the observed intensity, Y_c is the calculated intensity, $(Y_o - Y_c)$ are the background-corrected profile, NO is the number of observations, NV is the number of variables, and $(NO - NV)$ is the number of degrees of freedom. *CHISQ* is also referred to as the 'goodness of fit.' The 'goodness of fit' is a measure of how well the fitted model accounts for the data. For the SIROQUANT© program Taylor (1989) defines a *CHISQ* value that approaches 1.0 as a perfect fit, but that in general a value below 3.0 indicates a well refined pattern. Prince (1995) defines goodness of fit values >1.7 as a strong indication of model inadequacy or a false minimum. Prince states values <1.0 are an indication not of high quality refinement but of over parameterization. Residual errors caused by intensity aberrations tend to be both positive and negative. By using the full pattern these errors are resolved over the entire pattern leaving the scaling factors largely unchanged (Taylor and Matulis, 1991).

RIETVELD METHOD AND THE SIROQUANT© PROGRAM

The Rietveld refinement method is different from other more traditional techniques for evaluating X-ray powder diffraction data in that it uses digital diffraction data and is accomplished on a step-by-step basis, instead of utilizing individual reflections (Bish, 1993). Rietveld refinement minimizes the sum of the weighted squared differences between observed and calculated intensities at every 2θ step in a digital powder pattern.

Taylor (1991) calculates the intensities for the whole profile by using the formula for the intensity of a background-corrected point on the profile given by Rietveld (1969) for phase *a* (*K* is used to denote the triplet (hkℓ) and *(i)* is intensity): $y_{(i)}$ (calc) =

$$Scale_a \, \frac{1}{\mathrm{T}_a} \sum_{K(a)} J_{K(a)} \, F^2_{K(a)} \, (ANG)_a \, \frac{ASYM}{H_{K(a)}} \, (PREF_{K(a)}) \, (SHAPE) \, , \qquad (6)$$

where $Scale_a$ is the Rietveld scale of phase *a*; τ_a is the Brindley factor; $J_{K(a)}$ is the multiplicity factor; $F_{K(a)}$ is the structure factor; *ANG* is the angular factor that covers Lorentz and polarization effects; *ASYM* is the Rietveld (1969) line asymmetry function; $PREF_{k(a)}$ is the March-Dollase preferred orientation function;

$$PREF_{k(a)} = (r^2 \cos^2 \alpha + \sin^2 \alpha / r)^{-3/2}; \qquad (7)$$

and *SHAPE* is the line-shape function (Pearson VII),

$$SHAPE_{K(a)} = \left(1 + 4 \, (2^{\frac{1}{m}} - 1) \, \frac{(2\theta_i - 2\theta_K)}{H_K^2} \right)^{-m} , \qquad (8)$$

where the refineable parameter is *m*, which is 1 for Cauchy, 2 for modified Lorentzian, and ∞ for Gaussian.

Taylor and Matulis (1991) modified the SIROQUANT© program with the Brindley particle absorption factor (τ) to account for absorption effects. SIROQUANT© is one of the few programs that incorporates this factor into the calculation for quantitative analysis.

SIROQUANT© refinement begins with a reasonably accurate structure model. The diffraction data is then used to refine the model to yield an accurate agreement between the observed and calculated patterns. Additional information from chemical or transmission electron microscopy (TEM) data can help with the first guess (estimated) parameters. The Rietveld method uses the first guess parameters with an algorithm to minimize the difference between the predicted and the observed pattern. The SIROQUANT© program modifies the first guess parameters to new parameters which better fit the actual data. The Rietveld method propagates errors into the phase analysis results using the standard deviation of the scale factor of each phase estimated in the least squares refinement (Hill, 1991).

2 Θ STEP SIZE

Bish and Chipera (1995) found that a 2θ step size of ~20 times smaller than the full-width at half-maximum (FWHM) of the Kα peak yields reproducible peak positions when used in conjunction with profile fitting or Rietveld refinement. Jones and Malik (1994) also noted the need for small step sizes while performing curve-fitting. Hill (1995) suggested that as a rule of thumb the optimum step width should be between one-fifth and one-third of the minimum FWHM of the peaks. The 2θ step size used for this work of the minimum FWHM of the peaks. The 2θ step size used for this work was suggested by Jones, Bish, and Hill.

COUNTING TIME/INTENSITIES

Von Dreele and Cline (1995) stated that precision in quantitative analysis via powder diffraction methods was dependent only on the precision of diffraction intensity measurements. Counting statistics can affect these measurements by either producing insufficient or excessive data points needed for Rietveld analysis. Hill (1995) suggested that for refinement, an average of 10 thousand counts should be accumulated for the step intensities of the largest peaks of the pattern. Pattern intensities must be strong enough so that there is a clear distinction between the mineral phases and background levels. Strong pattern intensities are crucial when trace amounts are present (C.E. Matulis, pers. comm.). Taylor (1989) also suggested that if the presence or absence of a phase is ambiguous, corroboration by another method of analysis should be made.

REPRESENTATIVE SAMPLE

Sample homogeneity must be achieved when mixing the soil with the spike (Bish and Chipera, 1995). Bish and Chipera cautioned that the integrity of the specimen surface might be compromised during the preparation of the mount. Von Dreele and Cline (1995) found that the best method to blend samples was in an agate mortar using a kneading motion. They stated that achieving homogeneity in synthesized mixtures was difficult. Cline and Snyder (1987) discussed the care taken in grinding and preparing all of their samples. Brindley and Udagawa (1959) described how the integrity of the surface of a quartz sample was changed due to grinding and why the subsequent removal of an amorphous layer with 10% HF acid was necessary.

MOISTURE CONTENT

When performing X-ray analysis, environmental (moisture) conditions should be kept constant because moisture content can produce an "amorphous hump" in an X-ray pattern. Liquid has a structure almost completely lacking in periodicity, resulting in an X-ray pattern showing nothing more than one or two broad maxima (the "amorphous hump") (Cullity, 1978). The amount of moisture in a sample must be known when adding an internal standard (spike), because the weight percentage of the spike must be accurately determined.

Moisture content affects some minerals more than others. Among the clay-size minerals, smectite and vermiculite are the most affected by moisture because of their high shrink and swell properties (Hurlbut and Klein, 1977). Most of the minerals found in the soils used for this study were oxides which were not greatly affected by changes in moisture content during X-ray analysis.

SIROQUANT© PARAMETERS

Taylor (1989) ranked the refineable parameters in order of importance: 1) instrument zero, 2) linear halfwidth (W), 3) unit cell parameters (a, b, c, α, β, γ), 4) compensation for preferred orientation within the specimen, 5) peak shape factor (Pearson m), and 6) asymmetry. Note that quantitative analysis is dependent on the scale factor of each phase, therefore the scale factor parameter should constantly be refined. No change in the scale factor means no change in the calculated quantities, regardless of improvements in the fit.

STRUCT PROGRAM

Taylor (1991) described STRUCT, a sub program of SIROQUANT© which refines the structure factors F of a phase so that the relative intensity of the hkl peaks of a calculated pattern closely match the observed pattern. The structure program changes the relative intensities of the peaks by refining the positions of the atoms in the unit cell. In STRUCT, the variable structural parameters are atomic positions (x, y, z), atomic occupancies, and isotropic U values (temperature factors) of a phase which are estimated by least-squares fit to the observed pattern.

NON-CRYSTALLINE ALUMINOSILICATES AND HYDROUS OXIDES EXTRACTABLE BY ACID AMMONIUM OXALATE IN THE DARK (AOD) VERSUS RIETVELD CALCULATED AMORPHOUS PERCENTAGES

Although most soils consist primarily of crystalline minerals, many contain appreciable amounts of noncrystalline inorganic material (Jackson et al., 1986). Wada and Wada (1976) described noncrystalline Al, Fe, and Si material in various Hydrandepts. Fey and LeRoux (1977) stated that even small amounts of non-crystalline material in a soil can greatly affect the physical and chemical properties of that soil. For these reasons it is considered desirable to quantify and characterize the amorphous as well as the crystalline portions of soils (Jackson et al., 1986).

Prior to Rietveld analysis, selective dissolution analysis was the primary technique for the study of the amorphous component of soils. The main drawback of a chemical dissolution technique is that it is difficult to assess what portion of the soil is extracted. The acid ammonium oxalate in the dark (AOD) method was considered by most investigators to selectively dissolve only the noncrystalline materials (Fey and LeRoux, 1977). Schwertmann (1973) found that the AOD method also removes some short range ordered oxides and hydroxides of Al, Fe, and Mn. McKeague et al.

(1971) pointed out that the severity of this treatment increases with a decrease in particle size.

The fact that the severity of the AOD treatment increases with decreasing particle size needs to be considered when using the clay size fraction (<2μm) of soils.

AMORPHOUS MATERIAL DETERMINATION

The amorphous content can be calculated provided a highly crystalline "internal standard" is added to the sample prior to X-ray diffraction and Rietveld refinement. In the "internal standard" method of phase analysis, a known weight fraction W_s of a reference phase s is added to the mixture, and the abundance W_r of phase r is given by Klug and Alexander (1974):

$$W_r = \frac{W_s}{R_{rs}} \frac{I_r}{I_s} , \qquad (9)$$

where R_{rs} is the 'reference intensity ratio' of a reflection of phase r relative to a reflection from a standard phase s in the same mixture, I_r is the intensity of phase r, and I_s is the intensity of a standard phase s. The sum of W_r may be used to estimate the amount of amorphous material as follows:

$$W_{amorphous} = 1 - \sum_{r} W_r \,, \tag{10}$$

Taylor (1989) describes the method of amorphous material calculation. The SIROQUANT© method normalizes all crystalline components to 100%, discounting amorphous material content. Therefore, if a crystalline mineral, called a spike, is added to the sample in a precise amount, the amorphous material content can be estimated. Inasmuch as the spike is included in the 100% of all crystalline minerals, the spike will be reported in higher values than the amount that was added. In fact, all crystalline components will register higher than their true amounts if the percentage of amorphous material is not factored into the total analysis. The difference between the calculated amount of the spike and its actual content estimates the amount of amorphous material in the sample.

To achieve the best results, a sample must be X-rayed twice, with and without a spike. The dilution by the spike must also be accounted for (Taylor, 1989). The crystalline mineral percentages are refined for a non-spiked-sample; then the amorphous material content is estimated from a spiked sample using the parameters obtained from the non-spiked sample.

Taylor (1991) points out that amorphicity can be measured by adding an internal standard (spike), but this method cannot distinguish between amorphicity in the list of known phase, or amorphicity due to a further unlisted phase.

It is important to choose a spike that has little to no amorphous phase associated with it. Von Dreele and Cline (1995) calculated that alumina SRM 676 contains a 1.77 % amorphous component with an uncertainty of 0.68%.

CHARACTERISTIC RADIATION

When electrons that are accelerated from the filament of an X-ray tube strike the target with sufficient energy to ionize the inner electron shell of the target element, the vacancies are immediately filled by electrons that fall from outer shells of the element. The energy difference between the outer and inner electron shells is then released in the form of photons (X-rays) that are characteristic (in terms of energy/wavelength) of the target element (Moore and Reynolds, 1989). This energy is a function of the number of protons in the nucleus and is different for every element (Klug and Alexander, 1974). The energy emitted when an electron drops down to replace a missing electron is specific to the shell from which it came. For example, when an electron is displaced from the K shell, it is most often replaced by an electron from the L_3 shell which produces a characteristic (energy or wavelength) called the $K\alpha_1$.

The characteristic X-ray wavelength produced by the X-ray tube is chosen to be the same magnitude as the distance, d, between the atomic planes in crystalline materials. The relationship between crystalline atomic plane spacings, d, and the X-ray wavelength, λ, is given by the Bragg equation:

$$n \lambda = 2 d \sin \theta , \qquad (11)$$

where n is any whole number and is referred to as the order of the reflection. The incident and diffracted angles, θ, to any set of reflecting atomic planes must be such that the X-ray path-length between any two adjacent planes must be an integral number, n, of wavelengths, λ. This condition must be met to achieve X-ray diffraction.

In order to employ the Rietveld method the sample must be infinitely thick at a given wavelength, λ, at the highest diffraction angle, θ, that will be used for the analysis. Infinitely thick implies that in the sample the product of the total X-ray path length and the mass absorption will reduce the beam intensity reaching the detector to near zero.

Infinite thickness obeys Lambert's law:

$$I_\lambda = I_{0\lambda} \exp(-\mu^*_\lambda t_{total}) , \qquad (12)$$

where I_λ is the X-ray intensity of wavelength, λ, that will reach the detector; $I_{0\lambda}$ is the intensity of the incident beam at wavelength, λ; μ^*_λ is the total mass absorption of the sample at wavelength, λ; and t_{total} is the X-ray path length into and out of the sample at the highest diffraction angle, θ, that will be used for the analysis. When the product of t_{total} and μ^* approaches a maximum thickness, the exponential approaches zero. This causes the intensity I_λ, that reaches the detector to approach zero.

MATERIAL AND METHODS

SOILS

The soils for this experiment are listed in Table 1 together with their classification. Information regarding sampling, handling, and classification were taken from Jackman (1994). The Kaiwiki and Maile soils were collected from the island of Hawai‘i; the Ha‘iku, Moloka‘i and Pulehu soils from the island of Maui. The Wahiawa and Waialua soils are from the island of O‘ahu, and the Hali‘i, Kapa‘a, and Makapili soils are from the island of Kaua‘i. All soil samples were collected from the surface horizon, generally from a depth of 0 to 15 cm. The Kaiwiki sample was allowed to dry slightly, enough to allow the soil to pass a 6.3 mm (¼ inch) sieve. The Maile soil was allowed to dry until it could readily pass a 2-mm sieve. The remaining soils were air-dried and ground to pass a 2-mm sieve.

Table 1. Soil series and classifications.

Soil Series	Classification
Andisol	
Kaiwiki	Typic Hydrandept, thixotropic, isothermic (Typic Hydrudand, hydrous, isothermic)
Maile	Hydric Dystrandept, thixotropic, isomesic (Acrudoxic Hydrudand, hydrous, isohyperthermic)
Oxisol	
Hali'i	Typic Gibbsihumox, clayey, ferritic, isothermic (Anionic Acrudox, fine, ferritic, isohyperthermic)
Kapa'a	Typic Gibbsihumox, clayey, gibbsitic, isothermic (Anionic Acrudox, v.fine, sesquic, isohyperthermic)
Makapili	Typic Acrohumox, clayey, ferritic, isothermic (Anionic Acrudox, v.fine, sesquic, isohyperthermic)
Moloka'i	Typic torrox, clayey, kaolinitic, isohyperthermic (Typic Eutrotorrox, fine, kaolinitic, isohyperthermic)
Wahiawa	Tropeptic Eutrustox, clayey, kaolinitic, isothermic (Rhodic Eutrustox, v.fine, kaolinitic, isohyperthermic)
Ultisol	
Ha'iku	Humoxic Tropohumult, clayey, ferritic, isothermic (Typic Palehumult, clayey, oxidic, isohyperthermic)
Mollisol	
Pulehu	Cumulic Haplustoll, fine-loamy, mixed, isohyperthermic
Waialua	Typic Haplustoll, v.fine, kaolinitic, isohyperthermic

The classifications are according to the State of Hawai'i Soil Survey, Soil Survey Staff (1972; Soil Survey Staff (1973). Names in parentheses are the tentative classifications according to the 1992 revision of the Soil taxonomy (H. Ikawa, pers. comm.)
From Jackman (1994).

Most Hawaiian soils have high surface areas and contain hydroxides of Al and Fe and Fe and Al silicate gels. Two Andisols, the Kaiwiki and the Maile were selected because of their high amount of amorphous material (consisting mainly of Al and Fe gels). Five Oxisols were chosen for the experiment, three of which (Hali‘i, Kapa‘a and Makapili) were selected to give a range in relative percentages of Fe and Al hydroxides, ranging from predominantly Fe hydroxides (Hali‘i), to a soil with nearly equal percentage of Fe and Al hydroxides (Kapa‘a), to predominantly Al hydroxides (Makapili). The other two Oxisols were chosen because both contained large concentrations of kaolin (Moloka‘i) and one contained smectite (Wahiawa). One Ultisol (Ha‘iku) was chosen for its mica and smectite content. Two Mollisols were chosen, (Pulehu) and (Waialua), because both contain phyllosilicates.

CHEMICAL ANALYSIS OF SOILS

Oxalate Extraction

Oxalate extractable soil material is thought to contain most of the noncrystalline and quasicrystalline materials in soils, specifically the noncrystalline aluminosilicates and hydrous oxides (Jackson et al., 1986). A modified version of the ‘acid ammonium oxalate in the dark’ method by Jackson et al. was used to determine the extractable percentages of Si, Mn, Fe, and Al. The modification was that instead of washing the sample, the remaining oxalate solution was recorded and subtracted from the final weighing at 100°C. Soil samples were first treated with hydrogen peroxide to remove most of the organic carbon, the clay fraction was removed by ultrasonic dispersion and centrifugation, and was air dried and ground in an agate mortar. Manual grinding was chosen over mechanical grinding to minimize the possibility that amorphous material might be produced. A 0.15 g sample was mixed with 30 mL of 0.2M ammonium oxalate, adjusted to pH 3.0 with HCL, in a 50 mL centrifuge tube wrapped in aluminum foil. Light, especially ultraviolet light, causes ammonium oxalate to remove both crystalline and noncrystalline oxides of the soil and must be avoided. After 2 hours the sample was centrifuged and the supernatant liquid decanted. Differences between final weight (at 110°C) and initial weight was assumed to be the mass loss (of amorphous material) by dissolution of the ammonium oxalate. The oxalate supernatant liquid was analyzed for Si, Mn, Fe and Al concentration by ICAP analysis on a Perkin-Elmer Model 6500 Inductively Coupled Atomic Emission Spectrometer.

Total Elemental Analysis

Total elemental analysis was done by X-ray fluorescence spectroscopy on a Siemens SRS303 Wavelength Dispersive X-ray Fluorescence Analyzer.

Approximately 2 g of oven-dried clay-size fraction was weighed to 5 decimal places. The sample was then heated to 900°C and reweighed; the weight difference is the loss on ignition (LOI) and includes C, CO_2, S, Cl and structural water. Duplicate samples of 0.45000 ±0.0005 g of the ignited sample mixed with 2.95000 ±0.0002 g of lithium tetraborate were fused for 5 minutes at 900°C. The melt was swirled and pressed into glass disks for analysis.(Hulsebosch, pers. comm.)

QUANTITATIVE & QUALITATIVE MINERALOGICAL AND AMORPHOUS ANALYSIS

X-ray Diffraction

X-ray diffraction was utilized in the quantitative estimation of minerals in the clay fraction. Prior to analysis the soil samples were split into two sub samples. One part was treated with hydrogen peroxide. The clay-size fraction was separated by ultrasonic dispersion and centrifugation. The pH of the Kapa'a and the Makapili soils required adjustment for dispersion. Samples were air dried and ground in an agate mortar and pestle. Both samples (the peroxide treated and un-treated clay samples) were again split into two sub samples. The water content was determined by weighing one gram air-dried sample dried overnight at 105° C for 24 hrs x 3 replicates. Thirty percent by weight, corundum SRM 674 spike was added to a treated and un-treated sub sample and again mixed in the agate mortar. The samples were then packed into a zero background aluminum cavity mount which accommodates about a two-mm-thick specimen. Preferred orientation should be avoided when preparing samples by not pressing down too firmly when making the mounts. Previous trials have demonstrated that the samples were infinitely thick at the highest Bragg angle (80° 2Θ) used for this study. X-ray diffraction was conducted with a Philips Norelco diffractometer with a long fine-focus cobalt tube operated at 40 kV, 25 mA. The wavelength assumed for this study was $K\alpha$ 1.790260 Å (the average of $K\alpha_1$ 1.788965 and $K\alpha_2$ 1.792850 Å) (White and Johnson, 1970). A curved pytolitic-graphite monochrometer was employed in the diffracted beam as a $K\beta$ filter. Samples were run at varying integration times (04 and 10 seconds per step) to determine the difference in counting statistics for the sample. The divergent slit was set for a sample length of 2 cm (maximum coverage of the sample) at 4 degrees 2θ. Environmental conditions were kept at a constant temperature of 23° C and 55 % relative humidity. Intensities were collected at 0.025 degrees 2θ per step for a range of 4 to 80 degrees 2θ. The 2θ step size complies with the suggestions of Jones and Malik (1994) and Bish and Chipera (1995). Data were collected on disk as Hewlett Packard (HP) files and stored for future processing.

Rietveld Analysis

Rietveld analysis was done with a program called SIROQUANT© (Taylor, 1989) to estimate the percentages of the crystalline and amorphous material present in the clay fraction of both the hydrogen peroxide treated and non-treated samples. SIROQUANT© is a computer program that utilizes the Rietveld method to calculate a simulated pattern that is fit to the observed XRD pattern. Rietveld analysis utilizes a least squares refinement to fit the observed data to the simulate pattern, creating a unique scale factor for every data point. The scale factors are essential in estimating the mineral percentages of each phase. For a full explanation of the computer program see Taylor (1991). Before the XRD data can be utilized by SIROQUANT© the data must be formatted to match the needs of the SIROQUANT© program. A commercial program was purchased from Oswego Software (1984) to convert the XRD data from HP format to IBM PC format. A Fortran program was written by R.C. Jones to re-format the XRD files to match the requirements of the SIROQUANT© program. With the information from both XRF and Rietveld analysis, the oxide composition of both the crystalline and amorphous fractions can be estimated. By multiplying mineral percentages by their gravimetric factors the chemical composition of each crystalline phase was accounted for, and by difference the excess elemental oxide was allocated to the amorphous fraction. Gravimetric factors for specific minerals were calculated to account for atomic substitution within the lattice. The percentage of Al substitution for Fe in the crystal lattice of goethite was estimated by using formulas presented by Schulze and Schwertmann (1984), and Schulze (1984). For montmorillonite, calcium was used as the counter ion, as no sodium was detected by XRF. Twenty mole % reduction of potassium was assumed for illite.

Amorphous Material Oxide Composition by the Balance Sheet Method

A balance sheet method of combining X-ray fluorescence (XRF) data with XRD integrated intensities was employed to estimate ranges of mineral percentages in 11 Puerto Rican soils (Jones et al., 1982). The method allowed minimum and maximum percentages to be assigned to each mineral detected by XRD. In this study, a similar method was used to estimate the chemical composition of the amorphous material by assuming ideal and in some cases approximate mineral formulas.

Initially, the mineral percentages found by the Rietveld method were converted into their respective oxides by applying the respective gravimetric factors to the assumed mineral formulas. These values were then subtracted from the oxide values found by XRF. The remaining oxides were applied to the total oxide composition of the amorphous fraction including the remaining loss on ignition (LOI).

Weaver and Pollard (1973) noted, however that most soil minerals deviate from an ideal mineral formula. Therefore, the chemical compositions of the amorphous fractions of the study soils are considered estimates. Confidence in the assumed mineral formula of goethite is derived from Jones and Bish as reported by Bish (1993). They report that by using the mathematical formula of Schulze (1984) that the Kapa'a soil contained goethite very near the maximum Al for Fe substitution, about 30 mole %. XRD peak shifts have shown that goethite in other Hawaiian soils is highly substituted by Al. Therefore, the goethite gravimetric factors for the soils included in this thesis were based on 30 mole % Al substitution for Fe.

Moore and Reynolds (1989) noted that all illites have different chemical compositions and suggested that the determination of a reasonable stoichiometric formula for illite should start with the mineral formula for muscovite. They give the mineral formula for montmorillonite as $(Al_{1.67}Mg_{0,33})Si_4O_{10}(OH)_2R_{0.33}^{+}$ where R is the counter ion. Whenever smectite was encountered in Hawaiian soils, Ca was used as the counter ion inasmuch as Na is rarely found in detectable concentrations. Therefore, the counter ion for montmorillonite was taken as $R_{0.16}^{++}$.

Example of Balance Sheet Calculations

An example of the balance sheet method to find the difference between the total elemental concentration of each oxide and the contribution of the minerals in the Hali'i clay fraction follows. The example begins with the determination of the gravimetric factors for 30 mole % Al substituted goethite.

Molecular Weight of $Fe_{0.7}Al_{0.3}O(OH)$:

$0.7(55.8470)+0.3(26.9815)+15.9994+17.0074 = 80.1942$ and

$2(80.1942) = 160.3883$ (two formula units per unit cell).

Molecular Weight of Oxides in $Fe_{0.7}Al_{0.3}O(OH)$:

$Fe_2O_3 = 0.7(159.6922) = 111.7845$,

$Al_2O_3 = 0.3(101.9622) = 30.5887$, and

$H_2O = 18.054$.

Gravimetric Factors:

There are two (2) unit formulas in a unit cell: 80.1942 * (2) = 160.3883;

Multiply the mole percent Fe and Al (in $Fe_{0.7}Al_{0.3}O(OH)$) by the elemental oxides Fe_2O_3 and Al_2O_3 respectively, and the needed H_2O:

$Fe_2O_3 = MW(159.6922) * (0.7) = 111.7845$,

$Al_2O_3 = MW(101.9622) * (0.3) = 30.5887$,

$H_2O = 18.054$.

To calculate the gravimetric factors:

$$\frac{111.7845}{160.3886} = 0.69696 \textit{ for } Fe_2O_3 \qquad \text{and} \qquad 1 / 0.69696 = 1.43478,$$

$$\frac{30.5887}{160.3886} = 0.19072 \textit{ for } Al_2O_3 \qquad \text{and} \qquad 1 / 0.19072 = 5.24339,$$

$$\frac{18.0154}{160.3886} = 0.11232 \textit{ for } H_2O \qquad \text{and} \qquad 1 / 0.11232 = 8.90290.$$

Table 2 shows the calculations for 30 mole percent aluminum goethite:

Table 2. Gravimetric factors for 30 mole percent aluminum goethite

Constituent	Sought	Multiplier
goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	Fe_2O_3	0.69696
goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	Al_2O_3	0.19072
goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	H_2O	0.11232
Fe_2O_3	goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	1.43478
Al_2O_3	goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	5.24339
H_2O	goethite ($Fe_{0.7}Al_{0.3}O(OH)$)	8.90290

Rietveld analysis estimates the Hali'i clay fraction as containing 19.24% goethite, therefore:

19.24 * 0.69696 = 13.40951 (amount of Fe_2O_3 needed for 19.24% goethite),

19.24 * 0.19072 = 3.66945 (amount of Al_2O_3 needed for 19.24% goethite),

19.24 * 0.11232 = 2.16104 (amount of H_2O needed for 19.24% goethite).

The amount of Fe_2O_3, Al_2O_3, and H_2O (as loss on ignition, LOI) needed to create 19.24% goethite was subtracted from the total Fe_2O_3, Al_2O_3, and

H_2O found by X-ray fluorescence. The same gravimeteric calculations were done for all the crystalline constituents found by Rietveld analysis. The oxide components needed for the crystalline constituents were then subtracted from the total elemental percentages found by X-ray fluorescence. The difference between the total elemental oxides and the oxide crystalline percentages was assigned to the amorphous fraction of the clay.

Estimation of Amorphous Material and Correction of Crystalline Phase Weight Fractions

The Rietveld method of estimating the weight fractions of crystalline components is based on the normalization of all weight fractions to unity. The noncrystalline content is not considered in the normalization because the amorphous profile is fitted with a Rietveld background polynomial and removed from the pattern. If amorphous material is present, all crystalline values for weight fractions, including the weight fraction of an internal standard (spike), will be reported higher than their true values. To obtain reliable weight fraction estimates of the crystalline components and the amorphous material, two identical samples must be analyzed by X-ray diffraction: samples with and without an added spike. The over estimation of the spike weight fraction is used to estimate the preliminary total weight fractions of the crystalline and amorphous components in the following manner. The preliminary total weight fraction of the crystalline components, W'_{xtl}, is first found by:

$$W'_{xtl} = (W_s / W_{rs}) - W_s , \tag{13}$$

where W_s is the weight fraction of the added spike and W_{rs} is the weight fraction of the Rietveld reported spike. Note that in order to be valid, W_{rs} must be greater than W_s. The total weight fraction of the crystalline components, W'_{xtl}, does not include the added spike but does pertain to the sample in which the spike was added. Next, the preliminary estimate of the amorphous content is:

$$W'_{AM} = 1 - (W_s / W_{rs}) , \tag{14}$$

where W'_{AM} is the weight fraction of the amorphous component in the sample containing the spike. Because the spike acts as a diluent, a correction must be applied to remove the effect of the spike by:

$$F = 1 / (W'_{xtl} + W'_{AM}) , \tag{15}$$

where F is the dilution factor contributed by the spike.

Then:

$$F \cdot W'_{xtl} = W_{xtl} , \tag{16}$$

and

$$F \cdot W'_{AM} = W_{AM} , \tag{17}$$

where W_{xtl} is the sum of the crystalline weight fractions and W_{AM} is the weight fraction of the amorphous material with the spike dilution removed. It follows that $W_{xtl} + W_{AM} = 1$.

The weight fractions of the individual crystalline components, W_i, in the spiked sample must be corrected to their true values after the weight fraction of amorphous material has been estimated. Corrections are made by multiplying W'_i, the weight fractions of the crystalline phases found in the unspiked sample, by W_{xtl}. It follows that the amorphous material content, W_{AM}, is identical in both the spiked and unspiked samples, therefore, no further correction of W_{AM} is required. Each of the uncorrected crystalline weight fractions, W'_i, (found in the unspiked sample) are corrected by:

$$W^c_i = W_{xtl} \cdot W'_i , \tag{18}$$

where W^c_i is the corrected weight fraction of the ith component in a mixture of n phases. Therefore,

$$W_{xtl} = \sum_{I=1}^{n} W^c i \tag{19}$$

and the equality $W_{xtl} + W_{AM} = 1$ is maintained.

Example of Calculations for the Ha‘iku Soil

Table 3 lists the W_i for Ha‘iku soil.

Table 3. Ha‘iku soil (with spike)

Component	W_i	
Goethite	0.213	
Anatase	0.086	
Hematite	0.073	
Quartz	0.064	
Kaolinite	0.086	
Illite	0.412	
Gibbsite	0.049	
Smectite	0.018	
Corundum	0.473	(spike) W_{rs}
Total	1.000	

W_s = 0.2952 Corundum
The spike weight is not included in the total

$(W'_s / W_{rs}) - W_s = W'_{xtl}$ or $(0.2952 / 0.473) - 0.2952 = 0.3289 = W'_{xtl}$,

$1 - (W_s / W_{rs}) = W'_{AM}$ or $1 - (0.2952 / 0.473) = 0.3759 = W'_{AM}$,

$1 / (W'_{xtl} + W'_{AM}) = F$ or $1 / (0.3289 + 0.3759) = 1.4188 = F$

$F \cdot W'_{xtl} = W_{xtl}$ or $1.4188 \cdot 0.3289 = 0.4667 = W_{xtl}$,

$F \cdot W'_{AM} = W_{AM}$ or $1.4188 \cdot 0.3759 = 0.5333 = W_{AM} = 53.33\%$ amorphous material,

$W_{xtl} + W_{AM} = 0.4667 + 0.5333 = 1.$

Table 4 lists the W'_i and W^c_i for the Ha'iku soil.

Table 4. Ha'iku soil (no spike)

Component	W'_i	W^c_i
Goethite	0.213	0.099[†]
Anatase	0.086	0.040
Hematite	0.073	0.034
Quartz	0.064	0.030
Kaolinite	0.086	0.040
Illite	0.412	0.192
Gibbsite	0.049	0.023
Smectite	0.018	0.008
Total	1.001	$0.4660 = W_{xtl}$

$W_{xtl} \cdot W'_i = W^c_i$

[†] for example, $0.4667 \cdot 0.213 = 0.099 = W^c_i$ for goethite

RESULTS AND DISCUSSION

This investigation evaluated methods of soil sample preparation and the quality of amorphous material estimates attained by the Rietveld method. In conjunction with X-ray fluorescence analyses the Rietveld method was evaluated as a technique for the estimation of the chemical composition of the amorphous fraction.

METHODOLOGY STANDARDIZATION OF RIETVELD ANALYSIS FOR SOILS

Preferred Orientation

Preferred orientation was cited as the primary obstacle to acquiring accurate crystal structure data by Rietveld refinement (Bish and Chipera, 1995; Hill, 1995). Moore and Reynolds (1989) stated that preferred orientation in crystals was generally the result of prominent cleavage, or crystals with plate or rod-like morphology. Experiments utilizing X-ray diffraction have shown that when a greater number of crystal planes are lying in the direction of preferred orientation, the result will be an increased intensity of the diffraction peak. Will et al. (1983) stated that relatively few powder diffraction patterns were free of the effects of preferred orientation. If a correction for preferred orientation is not incorporated into Rietveld refinement, these diffraction peaks will result in a poorly fit X-ray diffraction pattern, resulting in inaccurate quantitative analysis and poor crystal structure refinement.

The SIROQUANT© program was chosen as the computer software to perform Rietveld analysis for this study. The program utilizes the March correction model to correct for the effects of preferred orientation during quantitative analysis (Taylor, 1991). Synthetic mixtures of SRM corundum 674 (2µm) and SRM silicon 640a (2µm) were prepared in ratios of 50:50, 30:70, and 70:30 percent by weight. The results are reported in Table 5.

Table 5. Effects of preferred orientation (PO) on the Rietveld determined analysis of silicon and corundum.

Weighed Amount g/Kg		Rietveld Calculated g/Kg			
		no PO[†] correction		PO[†] correction	
Silicon[‡]	Corundum[§]	Silicon	Corundum	Silicon	Corundum
234.5	765.5	248.0 ± 9.6	759.0 ± 9.1	241.7 ± 12.4	758.3 ± 12.4
303.8	696.2	319.3 ± 9.0	680.7 ± 8.5	316.0 ± 6.2	684.0 ± 6.2
500.0	500.0	515.0 ± 14.5	485.0 ± 14.5	506.7 ± 10.2	493.3 ± 10.2
498.9	501.1	503.0 ± 24.8	497.0 ± 24.8	505.0 ± 25.6	495.0 ± 25.6
771.1	228.9	795.7 ± 3.2	204.0 ± 3.6	798.0 ± 1.0	202.0 ± 1.0
694.5	305.5	697.7 ± 21.1	302.3 ± 21.1	697.0 ± 20.1	302.7 ± 20.3

[†] Preferred Orientation vector (104) for corundum SRM 674.
[‡] SRM silicon 640a.
[§] SRM corundum 674.
Results are the average of triplicate trials.

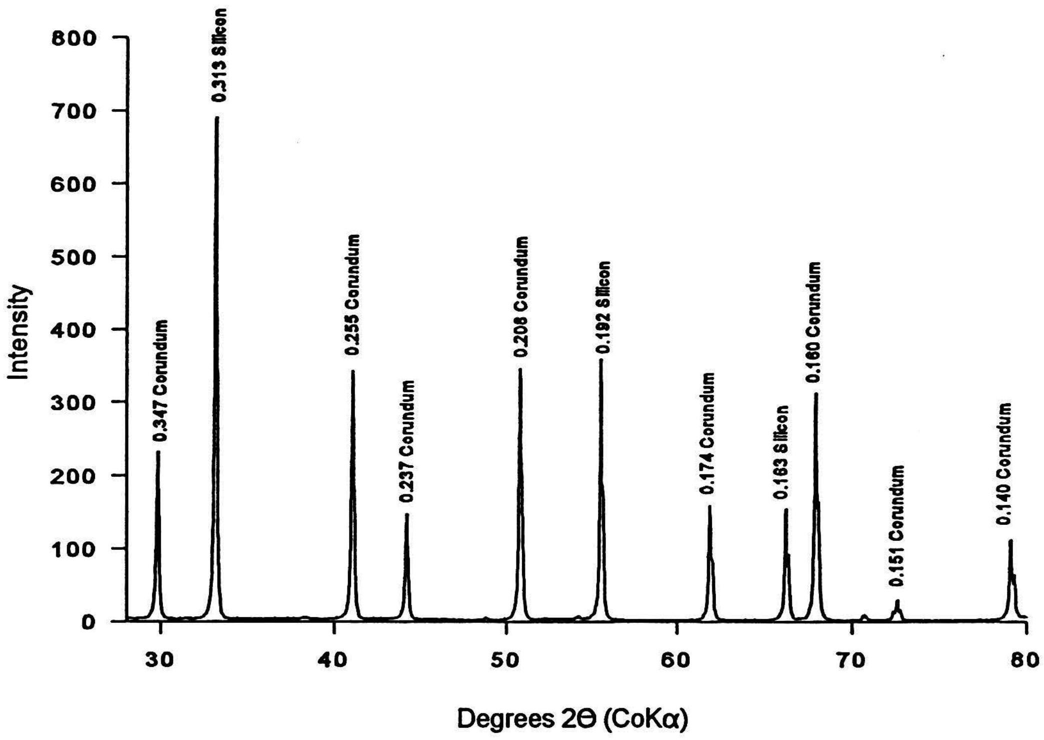
The results presented in Table 5 indicate there was no significant difference among calculated Rietveld results, whether the March correction was employed or not. The lack of significant difference was confirmed by utilizing the ANOVA statistical analysis package of Statistix 4.1(Analytical Software, 1994). ANOVA results are presented in Table 6.

Table 6. ANOVA statistics comparing preferred orientation and varying mineral level.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value	F-Critical
Varying mineral level	19.70	5	3.94	1.69	0.18	2.62
Orientation	0.49	1	0.49	0.21	0.65	4.26
Interaction	1.38	5	0.28	0.12	0.99	2.62
Within	56.04	24	2.34			
Total	77.61	35				

When comparing the Rietveld results of oriented mineral percentages versus unoriented mineral percentages, no significant difference was observed (P value 0.65). No significance was observed for the Rietveld calculated mineral percentages when the percentage levels of each mixture were varied (P value 0.18) and between the interaction of orientation and percentage levels (P value 0.99). The lack of significant difference in the calculated values can be explained by the fact that neither silicon nor corundum displayed much preferred orientation. Although the March correction was not necessary for the preceding trial, all soil samples showed a considerable degree of preferred orientation, making the March correction necessary.

The synthetic mixtures were intended to provide information as to whether corundum or silicon would best be used as an internal spike for amorphous content calculations. On examination of the X-ray diffraction pattern (Figure 1) indicated that because corundum had more diffraction peaks, Rietveld refinement would be enhanced by using corundum as a spike rather than silicon.



d spacing reported in nanometers.

Figure 1. 30% silicon : 70% corundum.

Hill (1995) conducted a similar experiment using rutile and corundum. His results showed a significant improvement in Rietveld calculated percentages by orienting corundum on the (104) vector and rutile on the (111) vector. Although the results of the present study did not agree with those of Hill, all further experiments utilized the orientation vector (104) for corundum as a precautionary measure.

Blending the Spike and Sample

Another important aspect of this experiment was to ascertain the homogeneity of the grinding and mixing methods. For this experiment samples were blended in an agate mortar using a kneading motion. This method was similar to that of Von Dreele and Cline (1995). Utilizing an optical microscope at 40X magnification, six samples were examined. Each of the six samples was then examined in triplicate (totaling 18 examined samples). For all 18 examinations, a distinct differentiation between the corundum and silicon particles was easily observed. Regardless of the fact that the samples did not appear homogeneous at 40X magnification, Rietveld percentages remained within ± 3% of the actual mineral percentages, which we considered sufficiently homogeneous.

Amount of Spike to Add

The SIROQUANT program permits the calculation of the overall amorphicity of a sample by comparing the amount of Rietveld calculated internal spike to the known amount of spike added to the sample. Taylor (1989) suggested adding 10-15 % by weight, because the spike lines might dominate the X-ray diffraction pattern. The example Taylor gave for the determination of Opal-CT used a 50 % by weight spike. Bish and Howard (1988) used 16.7 % by weight silicon as an internal standard to test the adequacy of Rietveld scale factors for multi-phase analysis, although in a later publication Bish and Chipera (1995) decided corundum would better serve as an internal spike because it afforded more diffraction peaks resulting in improved Rietveld fitting. Neither Taylor nor Bish and Howard presented a rationale for their choice of spike weight percentage. Further investigation was needed to determine what the appropriate amount of spike weight was needed to best estimate the amorphous content, and not overly dilute the crystalline portion of the sample. In order to evaluate the effect of spike weight on Rietveld amorphous content determination, R. C. Jones wrote a computer program that predicted the amount of amorphous material by comparing the calculated spike weight, W_{rs} , with the actual spike weight fraction, W_s.

The comparison was conducted between added spike levels of 10, 20, 30, 40, 50, 60, and 70% by weight with the indicated amorphous material levels at 1% increments for the increase of the Rietveld reported spike. Figure 2 shows the nonlinear relationship between the Rietveld reported spike percentage and the corresponding amount of amorphous material.

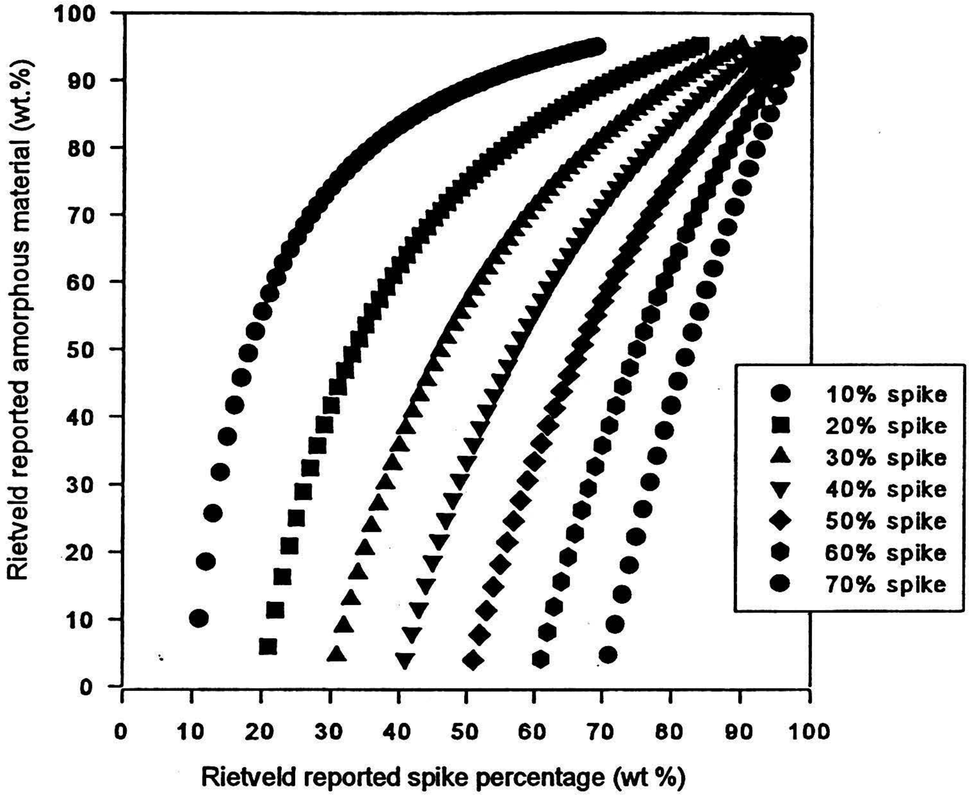


Figure 2. Estimation of amorphous material with varying amounts of spike.

Figure 2 shows that an optimum spike amount is dependent upon the amount of amorphous material present in the sample. At a 10% spike level, an increase from 11 to 12% in the Rietveld reported spike weight equates to a change of 10.10 to 18.52% in the Rietveld reported amorphous material, an increase of 8.42% calculated amorphous material. By contrast (also at the 10% spike level) when large amounts of amorphous material are present, an increase from 50 to 51% in the Rietveld reported spike percentage equates to only an 88.88 to 89.32% change in the amount of Rietveld reported amorphous material, an increase of 0.44% in the calculated amorphous material. The nonlinear nature of the 10% spike curve results in a very large increase in calculated amorphous material when small amounts are present, whereas a very small increase in calculated amorphous material results when large amounts of amorphous material are present.

Table 7 compares the change in the Rietveld reported spike percentage vs. the change in reported amorphous material.

Table 7. Change in Rietveld reported spike in addition to the added spike.

Added Spike (%)	Percent Change in Amorphous Material versus a 1% Incremental Change in the Rietveld Reported Spike						
	1 - 2 %	10 - 11 %	20 - 21 %	30 - 31 %	40 - 41 %	50 - 51 %	60 - 61 %
10	8.42	2.64	1.19	0.68	0.44	0.3	-
20	5.41	2.69	1.52	0.98	0.68	0.5	0.38
30	4.32	2.61	1.68	1.17	0.86	0.66	0.52
40	3.87	2.61	1.82	1.34	1.03	0.81	-
50	3.77	2.73	2.01	1.54	1.22	-	-
60	3.97	3.02	2.31	1.83	-	-	-
70	4.56	3.60	2.85	-	-	-	-

Table 7 numerically depicts the nonlinear nature of the rate of change of the calculated amorphous material percentage vs. a one percent incremental increase at various levels of the Rietveld spike. A 10% spike is a poor choice for very low levels of amorphous material but a 10% spike is a very good choice if the amorphous material levels are very high. Table 7 also shows that a 50% spike results in a small incremental change in the amount of calculated amorphous material at high levels, but experience has shown that a 50% spike provides excessive dilution. The calculated amorphous material in the study soils ranged from 35 to 87%, therefore, a spike was needed that could accommodate samples with medium to high amounts of amorphous material. A 30% spike is a compromise between 10 and 50% spikes in terms of the deviations in the calculated amorphous materials at relatively high levels (30% or more).

The average reported value for amorphous material present in the study soils was approximately 50%. Table 8 shows that when a sample contains 50% amorphous material a variation of 1% in the Rietveld reported spike changes the calculated amorphous percentage from 1.98 to 3.43 depending on the amount of spike added to the sample.

Table 8. Change in the percent amorphous material at the 50% level versus a Rietveld spike increase of 1%.

Added Spike (%)	Change in Rietveld Spike (%)	Increase in Reported Amorphous Material (%)	Difference (%)
10	18 to 19	49.38 to 52.63	3.25
20	33 to 34	49.24 to 51.47	2.23
30	46 to 47	49.69 to 51.67	1.98
40	57 to 58	49.71 to 51.73	2.02
50	66 to 67	48.48 to 50.75	2.27
60	75 to 76	49.99 to 52.63	2.64
70	82 to 83	48.78 to 52.21	3.43

With a 10% added spike, a change from 18 to 19% in the Rietveld reported spike percent changed the calculated amorphous material percentage from 49.38 to 52.63%, an increase of 3.25%. With a 30% added spike, a change from 46 to 47% in the Rietveld reported spike percent changed the calculated amorphous material percentage from 49.69 to 51.67%, an increase of 1.98%. With a 50% added spike, a change from 66 to 67% in the Rietveld spike percent changed the calculated amorphous material percentage from 48.48 to 50.75%, an increase of 2.27%. With a 70% added spike, a change from 82 to 83% in the Rietveld reported spike percent changed the calculated amorphous material percentage from 48.78 to 52.21%, an increase of 3.43%. Thus, the preceding examples illustrate that an added spike of 30% is an excellent compromise for the estimation of amorphous material percentages in the study soils.

Calculating Amorphous Percentages

Not many examples of amorphous content calculation utilizing Rietveld analysis can be found in the literature. We have seen many investigators utilizing Rietveld to analyze the internal structure of crystalline materials. In the SIROQUANT© manual (Taylor, 1989) presented the methodology for acquiring the amorphous percentage associated with an Opal-CT sample. With a minimum of input parameters the SIROQUANT© program can reveal the amorphous content of the sample. An example of the amorphous content calculations for one of the study soils is presented in the material and methods section of this thesis. Except for Taylor, others (Bish and Howard, 1988; Hill, 1991; Von Dreele and Cline, 1995), have also presented the basic methodology for the estimation of amorphous material, but they do not include the final calculation of the dilution effect of the spike.

The actual percentage of amorphous material present in a sample cannot be estimated without including the dilution factor of the spike.

Other basic questions regarding the capability of the Rietveld method to estimate amorphous content needed further investigation: Whether or not particle size affected the Rietveld calculation for amorphous content and how the amount of amorphous material affected the amorphous content calculation.

Varying Particle Size: Moderate Amounts of Amorphous Material

In the field of soil science the clay size fraction is defined as particles 2µm and smaller equivalent diameter. Therefore, the clay fraction consists of a range of particle sizes. In order to evaluate the ability of the Rietveld method to accurately estimate amorphous content regardless of a variation in particle sizes a petrographic glass slide was ground and sieved to <24µm and blended with SRM Silicon 640a which was certified as having a 2µm particle size. Samples were weighed and blended at a 50:50 glass to silicon ratio. The results are listed in Table 9.

Table 9. Actual versus Rietveld calculated amorphous (<24 µm glass) and crystalline (SRM silicon 640a <2 µm) percentages.

Actual Amounts		Rietveld Calculated Amounts[†]	
SRM silicon <2 µm	<24 µm glass	SRM silicon <2 µm	<24 µm glass
50.19	49.81	46.88	53.12
50.00	50.00	46.97	53.03
50.79	49.21	48.29	51.71
50.02	49.98	42.89	57.11
50.12	49.88	53.18	46.82
50.12	49.88	51.01	48.99

[†](30.06%, 30.00%, 30.73%, 31.03%, 31.25%, 30.75%) SRM corundum 674 oriented on (104) vector used for the estimation of amorphous material.

Rietveld reported results were within ± 7% of the actual amounts, which demonstrates that the ability of the Rietveld method to estimate the amorphous components in a crystalline sample is affected by a variation of particle sizes.

This experiment also indicates that there might be particle separation during sample preparation. The Rietveld calculated values for silicon (2µm) were consistently calculated as less than the actual value and the glass (<24µm) was calculated as more than was actually weighed.

Similar Particle Sizes: Large Amounts of Amorphous Material

Theoretically, up to 99.00% amorphous material can be calculated by the Rietveld method. In order to test whether or not large amounts of amorphous material could be accurately detected, a sample was prepared that was 95 % <2µm glass and 5% SRM Silicon 640a (2µm). Previous experiments have shown the inability of the Rietveld method to estimate amorphous materials of varying particle (24µm to 2µm) sizes. The results of this experiment are listed in Table 10.

Table 10. Actual versus Rietveld calculated amorphous (<2 µm glass) and crystalline (2µm SRM silicon 640a) percentages.

Actual Amounts		Rietveld Calculated Amounts[†]	
SRM silicon <2 µm	<2 µm glass	SRM silicon <2 µm	<2 µm glass
5.05	94.95	4.70	95.30

[†] (33.75%) SRM corundum 676 oriented on (104) vector.

Rietveld reported results within 1% of the actual amounts, which demonstrates the ability of the Rietveld method to closely estimate large amounts of an amorphous component in a sample.

Together, both this experiment and the previous one show that there is a difference in the ability of the Rietveld method to estimate the amorphous content of samples of varying particle size.

Both Bish and Chipera (1995) and Von Dreele and Cline (1995) state that 24µm is the maximum particle size that should be utilized for Rietveld analysis due to absorption.

Creating Amorphous Material During Sample Preparation

Because of a concern that amorphous material might be formed during grinding, a separate experiment was conducted. Brindley and Udagawa (1959) reported an amorphous coating on quartz as a result of grinding which posed a question as to whether or not amorphous material could be formed during sample preparation. To explore the possibility that crystalline phases may become amorphous during grinding, a quartz single-crystal was ground in a SPEX tungsten carbide ball mill to <24µm, spiked with 50% SRM corundum 674, and analyzed for amorphous content. Rietveld percentages were calculated using 49.97% corundum SRM 674 oriented on (104) vector. The Rietveld calculated amorphous material associated with the quartz sample was 17.37 ± 1.34% suggesting that indeed considerable amorphous material was generated by grinding. From the results of this experiment it appeared that grinding with the SPEX ball mill adversely affected the integrity of the sample surface during preparation.

Because the soils utilized for this study were separated by particle size using centrifugation, no grinding other than gently kneading of the sample in an agate mortar was needed to homogeneously mix in the spike.

The National Institute of Standards and Technology (NIST) is manufacturing a quartz sample (SRM quartz 1878a) with very little amorphous material associated with it. The amorphous layer is being removed with both HF and HCL. Before the removal of the amorphous fraction, the amount of amorphous material calculated by Rietveld analysis was reported to be approximately the same as our results (~17%) (James Cline, NIST Ceramics Division, pers. comm.). O'Connor and Raven (1988) report a quartz sample as containing an 18% amorphous component. Although these are only two reported values, these estimates for the amount of amorphous material associated with quartz are similar to those obtained in this experiment.

Amorphous material is associated with the particle surface and the particle surface area is proportional to particle size, i.e. the smaller the particle the greater the surface area, the greater the surface area; the more amorphous material.

More work is needed to determine if a given mineral will always have the same amount of amorphous material if the particle size is the same. Because grinding could occur by natural processes the answer to this question would be very useful for the estimation and characterization of amorphous material in soils.

INTEGRATION TIME

Estimated Standard Deviation (ESD)

Von Dreele and Cline (1995) state that precision in quantitative analysis via powder diffraction methods is dependent only on the precision of diffraction intensity measurements. Counting statistics can affect these measurements by either producing insufficient or excessive data points needed for Rietveld analysis. A series of experiments to determine the integration time needed for a sufficient number of data points was conducted. Table 11 shows the results obtained from the XRD patterns of the Hāli'i soil with two different integration times and two different spike levels.

Table 11. Rietveld percentages of the crystalline and amorphous fraction of the Hali'i clay size fraction with H_2O_2 treatment.

	30% Corundum[†] 04 seconds/step[§]	30% Corundum[†] 10 seconds/step[§]	50% Corundum[‡] 04 seconds/step[§]	50% Corundum[‡] 10 seconds/step[§]
Gibbsite	5.82 ± 0.54	5.64 ± 0.06	6.01 ± 0.08	5.65 ± 0.06
Quartz	3.60 ± 0.19	3.41 ± 0.04	3.64 ± 0.04	3.42 ± 0.04
Goethite	22.61 ± 1.19	21.44 ± 0.25	22.86 ± 0.29	21.46 ± 0.25
Hematite	3.00 ± 0.63	3.10 ± 0.03	3.30 ± 0.04	3.10 ± 0.04
Rutile	1.13 ± 0.06	1.07 ± 0.02	1.14 ± 0.02	1.07 ± 0.02
Anatase	5.67 ± 0.41	5.00 ± 0.06	5.33 ± 0.07	5.01 ± 0.06
Amorphous	58.13 ± 2.21	60.29 ± 0.46	57.67 ± 0.53	60.27 ± 0.47

[†] 30.22%, 30.28%,and 30.38% SRM Corundum 674 oriented on the (104) vector.

[‡] 50.10%, 49.88%,and 49.73% SRM Corundum 674 oriented on the (104) vector.

[§] Average of triplicate trials.

At the 30% corundum spike level, increasing the integration time from 4 to 10 seconds per step greatly improved the estimated standard deviation (ESD) of the counting statistics. Although the ESD improved, there was no significant change in the reported mineral percentages. The increase from 4 to 10 seconds per step resulted in doubling the amount of X-ray time from 5 ½ to 11 hours, which can be an inconvenience.

At the 50% corundum spike level, there was no significant change in the ESD by increasing the integration time from 4 to 10 seconds per step, and there was also no significant difference in the reported mineral percentages calculated between the 4 and 10 second trials.

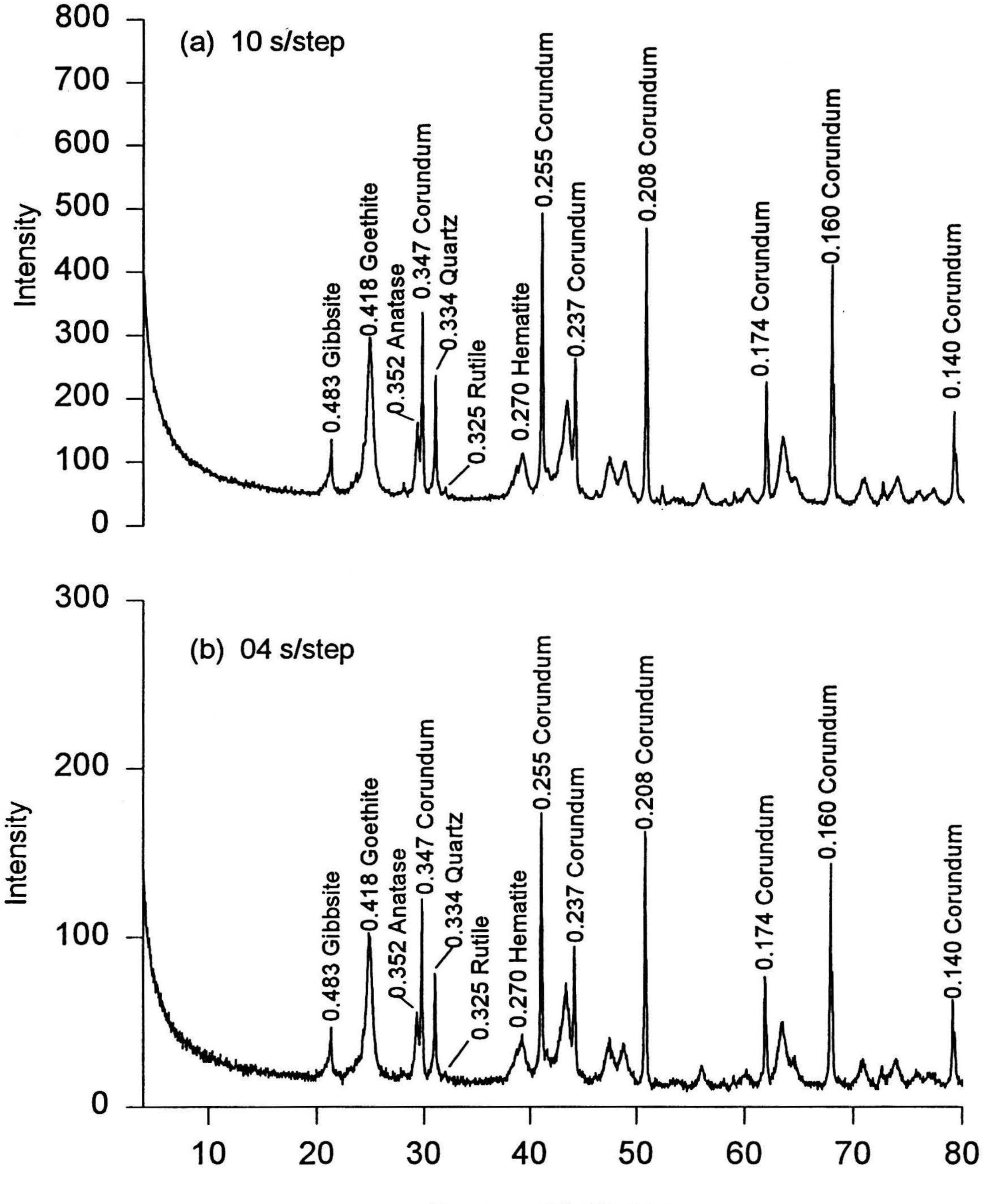
The reported ESD among the 10-second trial at the 30% spike level and the 4 - and 10 - second trials at the 50% spike level all showed a significant improvement in ESD over the 30% spike, 4 - second per step trial. Although the ESD improved for three of the trials, the reported mineral percentages in all four trials didn't change with amount of spike or integration time.

The lack of change in the reported mineral percentages for all four experiments suggests that the increase in integration time does not result in sufficient improvement in the results to recommend the use of 10 second per step over 4 seconds per step integration time.

The results of this experiment suggest a 30% spike at 4 seconds per step can acquire sufficient data points, a reasonable estimate of mineral percentages and an acceptable ESD for Rietveld analysis.

Dilution / Trace Mineral Levels

Dilution by the spike is illustrated by a comparison of the Hali‘i XRD patterns in Figures 3 (30% spike) and 4 (50% spike).



d spacing reported in nanometers.

Figure 3. Hali'i clay H_2O_2 treatment with 10 second/step integration (a) and 4 second/step integration (b) with 30% by weight corundum spike

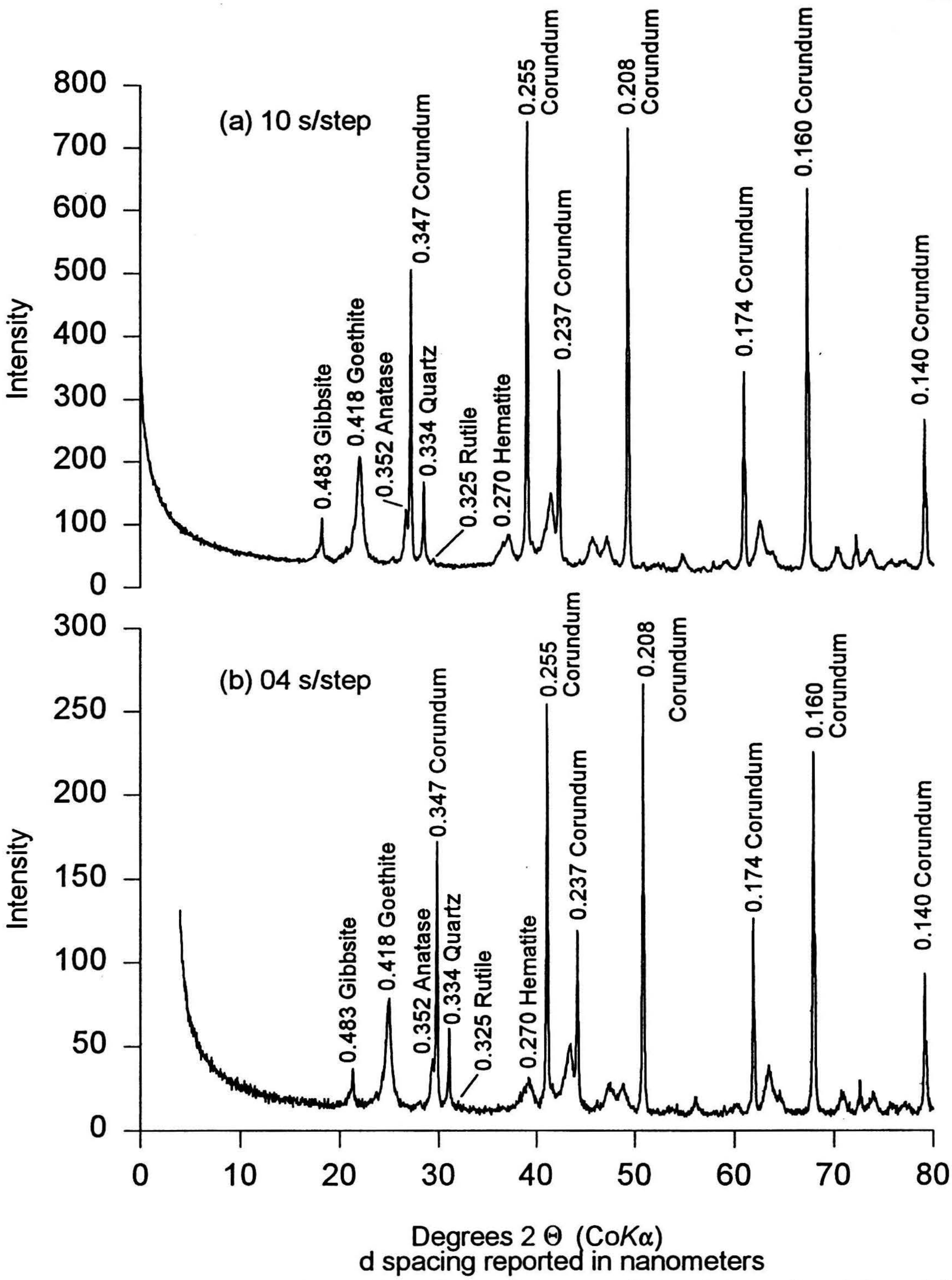


Figure 4. Hali'i clay H_2O_2 treatment with 10 second/step integration (a) and 4 second /step integration (b) with 50% by weight corundum spike

Figures 3 and 4 show a greater dilution by the 50% spike as compared to the 30% spike. The greater dilution causes an apparent improvement in the ESD because the fit of the Rietveld generated pattern to the observed pattern is closer for the 50% spike, because corundum (with higher intensity) is preferentially fit over the rest of the XRD pattern. Due to the dilution effect, the lower ESD for both the 4 and 10 second per step integration times of the 50% spike is a false indication of the ESD afforded by Rietveld refinement.

Dilution of the pattern by the spike can cause trace amounts of minerals to be obscured. For example, in Table 11 the average mineral percentage for rutile reported for in all 4 trials was 1.10 %. The rutile (110) peak for Hali'i in Figures 3a,b with the 30% spike is apparent in both the 4 and 10 seconds per step patterns. The rutile (110) peak in Figure 4a (the 50% spike at 10 seconds per step) is also apparent, but in Figure 4b (the 50% spike at 4 seconds per step) the peak cannot be distinguished from background noise which indicates that large spike amounts can dilute the sample to the extent that trace mineral amounts may be overlooked and removed with the background.

Even without the addition of a spike, the presence of trace levels of minerals can be difficult to detect by Rietveld analysis, but confirmation of the presence of a trace mineral can be made by chemical analysis. Hali'i displays a prominent 101 quartz peak yet the Rietveld reported mineral percentage for quartz is only 3.5 % (Figure 3 and Table 11.) None of the other soil constituents, (gibbsite, goethite, hematite, rutile, or anatase) contain Si in their chemical makeup, nor are there known reports in the literature where Si has isomorphicly substituted into the crystal lattice for any of these minerals. Chemical analysis of the soil as reported by X-ray fluorescence (XRF) confirmed the presence of Si. Taylor (1991) analyzed "pure rutile" by XRD with maximum intensities of 1000 counts. Besides rutile peaks, very low intensity zircon peaks were also observed. When Rietveld analysis was preformed, 1.4 % zircon was detected, the presence of which was then confirmed by chemical analysis.

APPLICATION TO SELECTED HAWAIIAN SOILS

Oxalate Extraction

Soil scientists commonly use oxalate extraction to measure the amount of "active" or easily extractable Fe and Al in soils. Although Schwertmann (1973) emphatically states that oxalate extraction does not remove the total amount of amorphous material in a sample, many investigators refer to the oxalate extractable portion of soils or minerals as the total amount of amorphous material. An experiment was undertaken in order to determine whether oxalate extraction and the Rietveld method would report the same amount of amorphous material. Table 12 compares the oxalate extractable percentages to the Rietveld calculated amorphous percentages from the H_2O_2-treated clay fraction of ten Hawaiian soils.

Table 12. Oxalate extractable percentages and Rietveld calculated amorphous percentages from the H_2O_2-treated clay fraction of ten Hawaiian soils.

	Oxalate Extractable Percentage	Rietveld Amorphous Percentage†
Hai'ku	20	53.2 ± 0.29
Hali'i	14	58.1 ± 2.21
Kaiwiki	58	85.7 ± 0.81
Kapa'a	13	44.1 ± 0.89
Maile	50	85.6 ± 0.91
Makapili	5	57.1 ± 1.63
Moloka'i	15	39.8 ± 3.31
Pulehu	10	65.2 ± 2.77
Wahiawa	11	35.0 ± 4.44
Waialua	18	58.3 ± 2.70

† Rietveld amorphous percentages calculated using corundum 674 oriented on the (104) vector.

The data collected indicate that Rietveld analysis will detect considerably more amorphous material than oxalate extraction. The increase in the amount of amorphous material detected could be caused by the nature of amorphous material.

In addition to discrete amorphous particles Jones and Uehara (1973) report that many amorphous oxides and hydrous oxides of aluminum and iron exist as coatings or gel-hulls on other particles, and perhaps these gel-hulls are not susceptible to oxalate extraction. Instead of amorphous particles or coatings, well crystalline particles could have amorphous areas on the surface. These localized areas of short-range order could be caused by internal crystal defects which extend to the surface. In soils, natural weathering processes could enhance these defects to form amorphous sites on the particles' surface.

Chemical Analysis of the Oxalate Extractant and the Chemical Composition of the Rietveld Calculated Amorphous Fraction

The relationship between the oxide composition of the amorphous material calculated by the Rietveld method and the oxide composition of the oxalate extractant was investigated to look for a correlation between the two. The oxide composition of the extractant was ascertained by ICAP, and the composition of the Rietveld reported amorphous material was calculated by the balance sheet method (see theory section). The oxides percentages of the oxalate extract and the oxide percentages as calculated by balance sheet method are illustrated in Table 13.

Table 13. Comparison of oxalate extraction analysis versus amorphous analysis as determined by Rietveld and XRF (the balance sheet method).

	Oxalate vs. Balance Sheet Analysis (BSA)			
	SiO_2	MnO	Fe_2O_3	Al_2O_3
Soil Series	% ox / % BSA [†]	% ox / % BSA	% ox / % BSA	% ox / % BSA
Ha'iku	0.05 / 6.47	0.02 / 0.06	2.02 / 22.65	0.48 / 6.10
Hāli'i	0.03 / 1.93	0.01 / 0.07	1.09 / 23.12	0.90 / 8.45
Kaiwiki	3.66 / 6.71	0.12 / 0.16	14.87 / 19.19	13.19 / 17.23
Kapa'a	0.04 / 5.73	0.02 / 0.06	1.47 / 13.36	0.84 / 10.45
Maile	1.96 / 4.21	0.27 / 0.23	9.60 / 11.78	10.17 / 10.99
Makapili	0.12 / 11.54	0.02 / 0.07	0.60 / 15.21	0.64 / 13.51
Moloka'i	0.26 / 11.37	0.17 / 0.34	0.51 / 3.48	0.54 / 10.69
Pulehu	1.33 / 16.72	0.13 / 0.29	2.01 / 9.27	2.50 / 13.47
Wahiawa	0.05 / 11.76	0.28 / 0.47	0.44 / 2.22	0.54 / 7.26
Waialua	0.23 / 19.89	0.38 / 0.21	0.87 / 12.48	0.72 / 10.24

[†] % ox: elemental analysis of oxalate extractable fraction. % XRF: elemental analysis as determined by Rietveld and XRF.

The data show no similarity in the amount of oxides reported by either method. The large variation between the oxalate extractable percentages and the Rietveld amorphous percentages, both in quantity and composition, suggests that the methods are measuring different portions of the soil. Although oxalate extraction was performed on the H_2O_2-treated clay fraction and XRF was performed on the untreated clay fraction, the comparison is reasonable because Rietveld analysis of the samples showed that H_2O_2 did little to change the composition of each.

H_2O_2 Treatment

The removal of organic matter utilizing H_2O_2 is standard practice in analytical soil science techniques (Kunze and Dixon, 1986). Organic matter has an aggregating effect and in some soils organic matter removal becomes necessary for dispersion. Rietveld mineral and amorphous percentages were calculated for the clay fraction of ten Hawaiian soils with, and without, H_2O_2-treatment to ascertain if the H_2O_2 affected the outcome of the results (Tables 14 and 15).

Table 14. Rietveld percentages of the crystalline and amorphous fraction of the clay from ten Hawaiian soils with H_2O_2-treatment.

					Soil Series					
	Ha'iku	Hali'i	Kaiwiki	Kapa'a	Maile	Makapili	Moloka'i	Pulehu	Wahiawa	Waialua
GOE	9.96 ± 0.06	22.61 ± 1.19	4.96 ±0.29	23.18 ± 0.37	2.85 ± 0.18	12.87 ± 0.49	-	-	-	-
GIB	2.29 ± 0.02	5.82 ± 0.54	1.17 ± 0.07	3.30 ± 0.06	2.66 ± 0.17	1.20 ± 0.05	1.75 ± 0.09	-	11.37 ± 0.78	-
MAG	-	-	1.61 ± 0.09	-	1.22 ± 0.08	-	-	-	-	-
QTZ	2.99 ± 0.02	3.60 ± 0.19	1.47 ± 0.09	1.23 ± 0.02	1.42 ± 0.09	ND‡	0.97 ± 0.05	-	1.30 ± 0.09	-
ANA	4.02 ± 0.03	5.67 ± 0.41	1.27 ± 0.07	3.35 ± 0.05	0.63 ± 0.04	1.67 ± 0.06	-	-	-	-
HEM	3.41 ± 0.03	3.00 ± 0.63	0.47 ± 0.03	-	0.54 ± 0.03	-	13.74 ± 0.76	2.12 ± 0.17	11.05 ± 0.76	2.13 ± 0.13
RUT	-	1.13 ± 0.06	-	-	-	-	-	-	-	-
KAO	4.02 ± 0.03	-	-	24.80 ± 0.40	-	27.15 ± 1.03	43.75 ± 2.40	32.66 ± 2.61	40.43 ± 2.76	39.02 ± 2.53
ILM	-	-	0.63 ± 0.04	-	1.10 ± 0.07	-	-	-	-	-
ILL	-	-	2.68 ± 0.15	-	3.87 ± 0.25	-	-	-	-	-
CRIST	-	-	-	-	0.16 ± 0.01	-	-	-	-	-
MUSC	19.27 ± 0.12	-	-	-	-	-	-	-	-	-
MONT	0.84 ± 0.01	-	-	-	-	-	-	-	0.85 ± 0.06	0.58 ± 0.04
AMOR†	53.24 ± 0.29	58.13 ± 2.21	85.74 ± 0.81	44.14 ± 0.89	85.55 ± 0.91	57.10 ± 1.63	39.75 ± 3.31	65.22 ± 2.77	35.01 ± 4.44	58.27 ± 2.70
SUM	**100.04**	**99.96**	**100.00**	**100.00**	**100.00**	**99.99**	**99.95**	**100.00**	**100.01**	**100.00**

†Corundum oriented on the (104) vector for amorphous calculation.

‡None detected

Results are the average of triplicate trials.

GOE-Goethite, GIB-Gibbsite, MAG-Magnetite, QTZ-Quartz, ANA-Anatase, HEM-Hematite, RUT-Rutile, KAO-Kaolinite, ILM-Illmenite, ILL-Illite, CRIST-Cristobalite, MUSC-Muscovite, MONT-Montmorillonite, AMOR-Amorphous

Table 15. Rietveld percentages of the crystalline and amorphous fraction of the clay from ten Hawaiian soils w/o H_2O_2-treatment.

	Soil Series									
	Ha'iku	Hali'i	Kaiwiki	Kapa'a	Maile	Makapili	Moloka'i	Pulehu	Wahiawa	Waialua
GOE	9.29 ± 0.16	19.24 ± 0.59	6.05 ±0.24	19.61 ± 0.80	2.46 ± 0.05	14.82 ± 0.12	-	-	-	-
GIB	1.65 ± 0.03	4.90 ± 0.15	1.08 ± 0.04	3.61 ± 0.15	1.83 ± 0.04	1.27 ± 0.01	0.81 ± 0.03	-	12.69 ± 0.37	-
MAG	-	-	1.95 ± 0.08	-	1.13 ± 0.02	-	-	-	-	-
QTZ	3.47 ± 0.06	2.96 ± 0.09	1.26 ± 0.05	1.19 ± 0.05	1.25 ± 0.02	0.27 ± 0.01	0.87 ± 0.03	-	0.69 ± 0.02	-
ANA	4.25 ± 0.07	5.84 ± 0.18	1.13 ± 0.05	3.71 ± 0.15	1.83 ± 0.04	2.86 ± 0.02	-	-	-	-
HEM	3.91 ± 0.07	3.11 ± 0.10	0.45 ± 0.02	-	0.17 ± 0.01	-	12.37 ± 0.49	1.94 ± 0.05	11.80 ± 0.34	1.76 ± 0.08
RUT	-	1.38 ± 0.05	-	-	-	-	-	-	-	-
KAO	3.78 ± 0.07	-	-	21.39 ± 0.87	-	26.11 ± 0.22	44.00 ± 1.73	31.48 ± 0.73	43.32 ± 1.26	34.69 ± 1.58
ILM	-	-	1.06 ± 0.04	-	1.14 ± 0.03	-	-	-	-	-
ILL	-	-	3.12 ± 0.12	-	3.27 ± 0.07	-	-	-	-	-
CRIST	-	-	-	-	0.20 ± 0.01	-	-	-	-	-
MUSC	16.05 ± 0.28	-	-	-	-	-	-	-	-	-
MONT	0.95 ± 0.01	-	-	-	-	-	-	-	0.55 ± 0.02	0.26 ± 0.01
AMOR†	56.61 ± 0.76	62.57 ± 1.14	83.90 ± 0.63	50.49 ± 2.01	86.71 ± 0.26	54.67 ± 0.38	41.95 ± 2.28	66.59 ± 0.77	31.02 ± 2.01	63.15 ± 1.87
SUM	**99.96**	**100.00**	**100.00**	**100.00**	**99.99**	**100.00**	**100.00**	**100.01**	**100.07**	**98.86**

†Corundum oriented on the (104) vector for amorphous calculation.
Results are the average of triplicate trials.
GOE-Goethite, GIB-Gibbsite, MAG-Magnetite, QTZ-Quartz, ANA-Anatase, HEM-Hematite, RUT-Rutile, KAO-Kaolinite, ILM-Illmenite, ILL-Illite, CRIST-Cristobalite, MUSC-Muscovite, MONT-Montmorillonite, AMOR-Amorphous

The Rietveld reported percentages for both the H_2O_2-treated and non-treated samples are all within experimental error, suggesting that any difference between the H_2O_2 treated soils and the untreated soils are due to sample variation and not treatment.

Blume and Schwertmann, (1969); McKeague et al., (1971); McKeague and Day, (1966) all found that aluminum and iron are associated with organic matter complexes. The lack of a significant difference among the samples indicates that the H_2O_2 treatment did not release any amorphous aluminum and iron associated with organic complexes, and that only the amount of C was reduced by H_2O_2.

Mineral Allocation by Balance Sheet

Various approaches have been used in an attempt to characterize the amorphous material in soils. Tazaki et al. (1989) made a lengthy and thorough investigation of a gel found in sand dunes. The gel was studied by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) with energy Dispersive X-ray spectrometer (EDX), scanning auger multiprobe (SAM), and X-ray photoelectron spectroscopy (XPS) in an attempt to characterize the material. Among other things this study points out the difficulties in isolating the amorphous fraction of soils for qualitative analysis.

There currently is no one method that has unequivocal acceptance as the method for amorphous characterization. The balance sheet method was designed to be a relatively inexpensive and uncomplicated method to perform characterization of amorphous material. The balance sheet method provides a first approximation as to the chemical constituents of amorphous material. The balance sheet utilizes both Rietveld analysis and XRF. A more in-depth discussion is found in the material and methods section.

Rietveld determines the total amount of amorphous material present but does not estimate how much amorphous material is contributed by each phase (Bish and Chipera, 1995; Hill, 1995; Taylor, 1991; Young, 1995). Both the crystalline and amorphous Rietveld percentages combined with XRF chemical analysis provides this means.

The mineralogical composition of the crystalline fraction and the chemical composition amorphous fraction for the clay of ten Hawaiian soils are illustrated in Tables 16-25. The soils have been presented in alphabetical order.

Table 16. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Ha'iku soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI [†]	Total	Rietveld [‡] %
Clay[§]	19.57	6.16	16.82	33.03	0.06	0.62	0.14	0.00	2.20	0.40	19.94	98.94	
Goethite	--	--	1.77[¶]	6.47	--	--	--	--	--	--	1.04	9.28	9.29±0.16
Anatase	--	4.25	--	--	--	--	--	--	--	--	--	4.25	4.25±0.07
Hematite	--	--	--	3.91	--	--	--	--	--	--	--	3.91	3.91±0.07
Quartz	3.47	--	--	--	--	--	--	--	--	--	--	3.47	3.47±0.06
Kaolin	1.76	--	1.49	--	--	--	--	--	--	--	0.53	3.78	3.78±0.07
Muscovite	7.26	--	6.16	--	--	--	--	--	1.90	--	0.73	16.05	16.05±0.28
Gibbsite	--	--	1.08	--	--	--	--	--	--	--	0.57	1.6	1.65±0.03
Montmorillonite[#]	0.61	--	0.22	--	--	0.03	0.05	--	--	--	0.05	0.96	0.95±0.01
Amorphous (by difference and Rietveld method)	6.47	1.91	6.10	22.65	0.06	0.59	0.09	0.00	0.30	0.40	17.02	55.59	56.61±0.76 99.96

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

[#] $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2Ca_{0.16}$

Table 17. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Hali'i soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	4.89	7.07	15.32	39.64	0.07	0.16	0.08	0.00	0.14	0.35	29.77	97.49	
Gibbsite	--	--	3.20	--	--	--	--	--	--	--	1.70	4.90	4.90±0.15
Quartz	2.96	--	--	--	--	--	--	--	--	--	--	2.96	2.96±0.09
Goethite	--	--	3.67[¶]	13.41	--	--	--	--	--	--	2.16	19.24	19.24±0.59
Hematite	--	--	--	3.11	--	--	--	--	--	--	--	3.11	3.11±0.10
Rutile	--	1.38	--	--	--	--	--	--	--	--	--	1.38	1.38±0.05
Anatase	--	5.84	--	--	--	--	--	--	--	--	--	5.84	5.84±0.18
Amorphous (by difference and Rietveld method)	1.93	0.00	8.45	23.12	0.07	0.16	0.08	0.00	0.14	0.35	25.91	60.21	62.57±1.14 100.00

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

Table 18. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Kaiwiki soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	9.38	4.49	20.29	26.31	0.16	0.43	0.10	0.00	0.39	0.85	37.18	99.58	
Goethite	--	--	1.15[¶]	4.22	--	--	--	--	--	--	0.68	6.05	6.05±0.24
Gibbsite	--	--	0.71	--	--	--	--	--	--	--	0.37	1.08	1.08±0.04
Magnetite	--	--	--	1.95	--	--	--	--	--	--	--	1.95	1.95±0.08
Quartz	1.26	--	--	--	--	--	--	--	--	--	--	1.26	1.26±0.05
Illite	1.41	--	1.20	--	--	--	--	--	0.37	--	0.14	3.12	3.12±0.12
Anatase	--	1.13	--	--	--	--	--	--	--	--	--	1.13	1.13±0.05
Hematite	--	--	--	0.45	--	--	--	--	--	--	--	0.45	0.45±0.02
Ilmenite	--	0.56	--	0.50	--	--	--	--	--	--	--	1.06	1.06±0.04
Amorphous (by difference and Rietveld method)	6.71	2.80	17.23	19.19	0.16	0.43	0.10	0.00	0.02	0.85	35.99	83.48	83.90±0.63
													100.00

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

Table 19. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Kapa´a soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	16.88	3.41	25.00	27.03	0.06	0.23	0.03	0.00	0.41	0.34	26.78	100.17	
Kaolin	9.96	--	8.45	--	--	--	--	--	--	--	2.99	21.40	21.39 ±0.87
Goethite	--	--	3.74[¶]	13.67	--	--	--	--	--	--	2.20	19.61	19.61±0.80
Quartz	1.19	--	--	--	--	--	--	--	--	--	--	1.19	1.19±0.05
Anatase	--	3.41	--	--	--	--	--	--	--	--	--	3.41	3.71±0.15
Gibbsite	--	--	2.36	--	--	--	--	--	--	--	1.25	3.61	3.61±0.15
Amorphous (by difference and Rietveld method)	5.73	0.00	10.45	13.36	0.06	0.23	0.03	0.00	0.41	0.34	20.34	50.95	50.49±2.01
													100.00

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

Table 20. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Maile soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	7.14	2.66	13.92	15.33	0.23	0.39	1.12	0.00	0.33	1.03	56.15	98.3	
Goethite	--	--	0.47[¶]	1.71	--	--	--	--	--	--	0.28	2.46	2.46±0.05
Gibbsite	--	--	1.20	--	--	--	--	--	--	--	0.63	1.83	1.83±0.04
Magnetite	--	--	--	1.13	--	--	--	--	--	--	--	1.13	1.13±0.02
Quartz	1.25	--	--	--	--	--	--	--	--	--	--	1.25	1.25±0.02
Illite	1.48	--	1.26	--	--	--	--	--	0.31[#]	--	0.15	3.20	3.27±0.07
Anatase	--	1.83	--	--	--	--	--	--	--	--	--	1.83	1.83±0.04
Hematite	--	--	--	0.17	--	--	--	--	--	--	--	0.17	0.17±0.01
Ilmenite	--	0.60	--	0.54	--	--	--	--	--	--	--	1.14	1.14±0.03
Cristobalite	0.20	--	--	--	--	--	--	--	--	--	--	0.20	0.20±0.01
Amorphous (by difference and Rietveld method)	4.21	0.23	10.99	11.78	0.23	0.39	1.12	0.00	0.02	1.03	55.09	85.09	86.71±0.26 99.99

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by x-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

[#] 20 mole % reduction potassium assumed.

Table 21. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Makapili soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld [‡] %
Clay[§]	23.96	2.98	27.48	25.54	0.07	0.14	0.29	0.00	0.15	0.28	19.66	100.55	
Goethite	--	--	2.83[¶]	10.33	--	--	--	--	--	--	1.66	14.82	14.82±0.12
Anatase	--	2.86	--	--	--	--	--	--	--	--	--	2.86	2.86±0.02
Gibbsite	--	--	0.83	--	--	--	--	--	--	--	0.44	1.27	1.27±0.01
Quartz	0.27	--	--	--	--	--	--	--	--	--	--	0.27	0.27±0.01
Kaolin	12.15	--	10.31	--	--	--	--	--	--	--	3.64	26.10	26.11±0.22
Amorphous (by difference and Rietveld method)	11.54	0.12	13.51	15.21	0.07	0.14	0.29	0.00	0.15	0.28	13.92	55.23	54.67±0.38 100.00

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] 30 mole % aluminum substituted for iron in the crystal lattice.

Table 22. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Moloka'i soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI [†]	Total	Rietveld [‡] %
Clay[§]	32.72	2.33	28.60	15.85	0.34	0.44	0.66	0.00	0.81	0.37	17.97	100.09	
Quartz	0.87	--	--	--	--	--	--	--	--	--	--	0.87	0.87±0.03
Kaolin	20.48	--	17.38	--	--	--	--	--	--	--	6.14	44.00	44.00±1.73
Gibbsite	--	--	0.53	--	--	--	--	--	--	--	0.28	0.81	0.81±0.03
Hematite	--	--	--	12.37	--	--	--	--	--	--	--	12.37	12.37±0.49
Amorphous (by difference and Rietveld method)	11.37	2.33	10.69	3.48	0.34	0.44	0.66	0.00	0.81	0.37	11.55	42.04	41.95±2.28 100.00

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

Table 23. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Pulehu soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	31.37	1.97	25.90	11.21	0.29	0.72	1.84	0.00	0.55	0.86	25.28	99.99	
Kaolin	14.65	--	12.43	--	--	--	--	--	--	--	4.39	31.47	31.48±0.73
Hematite	--	--	--	1.94	--	--	--	--	--	--	--	1.94	1.94±0.05
Amorphous (by difference and Rietveld method)	16.72	1.97	13.47	9.27	0.29	0.72	1.84	0.00	0.55	0.86	20.89	66.58	66.59±0.77 100.01

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for mineral and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

Table 24. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Wahiawa soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI[†]	Total	Rietveld[‡] %
Clay[§]	32.96	1.54	32.79	14.02	0.47	0.66	0.05	0.00	1.91	0.08	16.81	101.29	
Kaolin	20.16	--	17.11	--	--	--	--	--	--	--	6.05	43.32	43.32±1.26
Quartz	0.69	--	--	--	--	--	--	--	--	--	--	0.69	0.69±0.02
Gibbsite	--	--	8.29	--	--	--	--	--	--	--	4.40	12.69	12.69±0.37
Hematite	--	--	--	11.80	--	--	--	--	--	--	--	11.80	11.80±0.34
Montmorillonite[¶]	0.35	--	0.13	--	--	0.02	0.03	--	--	--	0.03	0.56	0.55±0.02
Amorphous (by difference and Rietveld method)	11.76	1.54	7.26	2.22	0.47	0.64	0.02	0.00	1.19	0.08	6.33	31.51	31.02±2.01
													100.07

[†] Loss on ignition; weight loss between 110°C and 900°C.

[‡] Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

[§] Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

[¶] $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2Ca_{0.16}$

Table 25. Chemical and mineralogical composition of the crystalline and amorphous fraction of clay (w/o H_2O_2 treatment) from the Waialua soil series.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI†	Total	Rietveld ‡ %
Clay§	36.21	1.80	24.00	14.24	0.21	0.90	0.80	0.00	0.37	0.50	21.79	100.82	
Kaolin	16.15	--	13.70	--	--	--	--	--	--	--	4.84	34.69	34.69±1.58
Hematite	--	--	--	1.76	--	--	--	--	--	--	--	1.76	1.76±0.08
Montmorillonite¶	0.17	--	0.06	--	--	0.01	0.01	--	--	--	0.01	0.26	0.26±0.01
Amorphous (by difference and Rietveld method)	19.89	1.80	10.24	12.48	0.21	0.89	0.79	0.00	0.37	0.50	16.94	64.11	63.15±1.87 99.86

† Loss on ignition; weight loss between 110°C and 900°C.

‡ Triplicate values for crystalline and amorphous percentages calculated by the Rietveld method.

§ Oxide analysis by X-ray fluorescence (±5% relative error based on multiple analysis of standard samples).

¶ $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2Ca_{0.16}$

In all cases XRF analysis provided sufficient and often abundant oxide components to formulate the Rietveld calculated crystalline percentages. If, for example, the Rietveld method calculated more quartz than XRF calculated SiO_2, the methodology would be in question. In all cases the XRF values were equal to or more than the crystalline percentages predicted by the Rietveld method. Once all the crystalline percentages are formulated the excess oxide components and water are assigned to the amorphous fraction. In all the soils in this study a large amount of water is assigned to the amorphous fraction.

All of the amorphous percentages calculated by Rietveld and by the balance sheet method are all within experimental error of each other. The difference between the two values is probably caused by an analytical discrepancy where the total reported by XRF or Rietveld is not necessarily 100 percent.

When calculating amorphous material another concern is the addition of amorphous material associated with the internal spike. Von Dreele and Cline (1995) calculated the amount of amorphous material associated with SRM corundum 676 as 1.77% with an uncertainty of 0.68%, as calculated by quantitative Rietveld analysis neutron time of flight data.

For this study SRM corundum 674 was used (rather than 676) so the exact amount of amorphous material added from SRM corundum 674 is not known. However, the amount of amorphous material in corundum is considered to be inconsequential relative to the amount of amorphous material present in the soil.

QUANTITATIVE ANALYSIS: AN ANALYSIS OF ERRORS

The quality of amorphous material estimates is directly dependent upon the ability to estimate the total crystalline fraction including the added spike. In the final result the total of all crystalline components plus the amorphous fraction must equal 100%. Thus, if there is a serious error in the determination of any one crystalline phase, all other phases including the spike will be affected. Consequently an error in the spike determination will result in a poor estimate of the amount of amorphous material. The quality of amorphous material estimates is, therefore, directly dependent upon the caliber of the crystalline phase estimates which in turn are dependent upon: 1) the integrity of the $hk\ell$ structure factors ($F_{hk\ell}$), 2) the ability to compensate for preferred orientation, 3) the ability to correct for phase differences in microabsorption, 4) the precision with which background is removed, and 5) the severity of the misfit of the peaks produced by the phyllosilicates. Figure 5 shows the observed, calculated and difference patterns resulting from the SIROQUANT© refinement of the XRD pattern for the Waialua clay fraction.

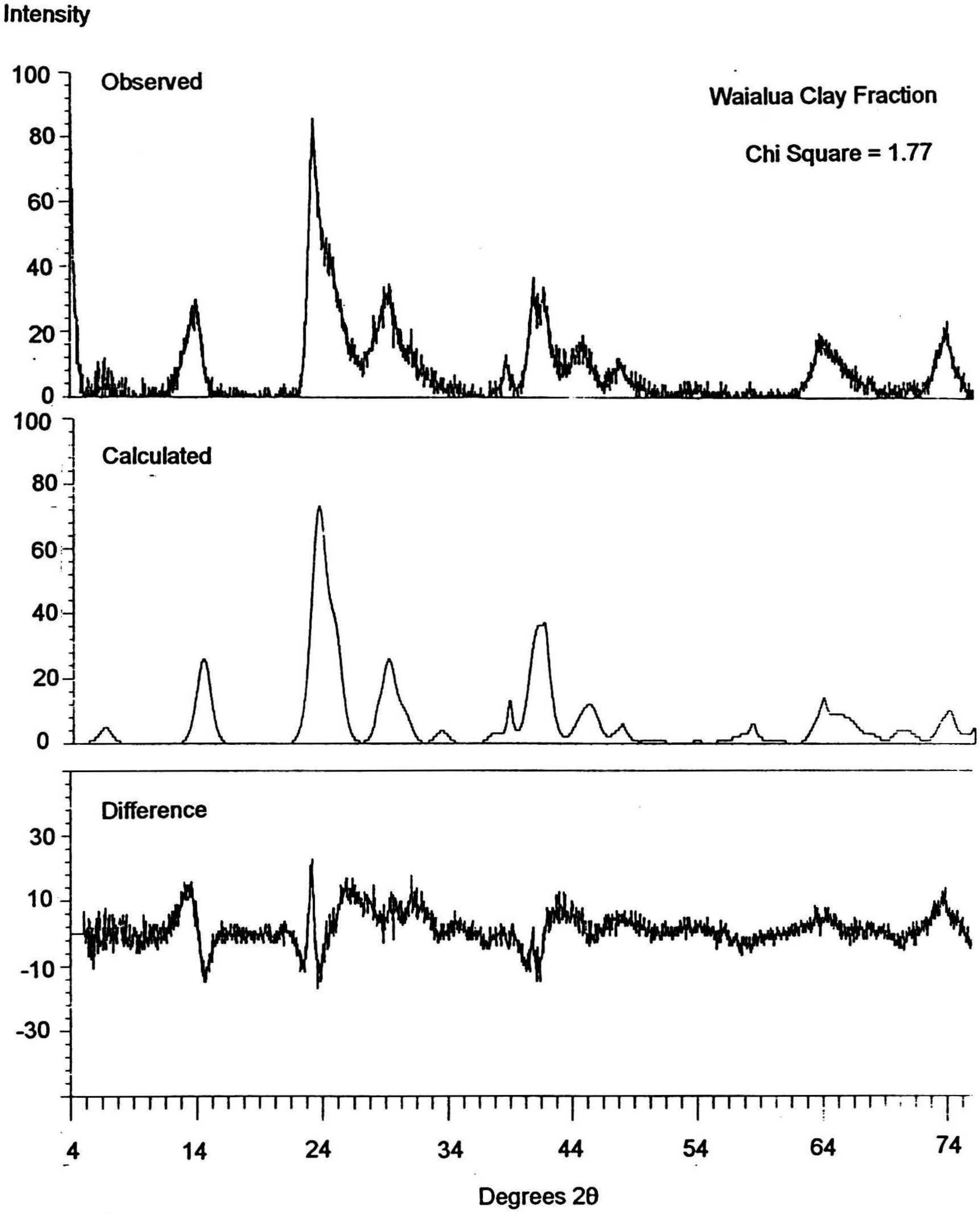


Figure 5. SIROQUANT© refinement of the XRD pattern for the Waialua clay fraction.

The Waialua clay fraction consists of kaolinite, hematite and montmorillonite. Figure 6 shows the observed, calculated and difference patterns resulting from the SIROQUANT© refinement of the XRD pattern for the Hali'i clay fraction.

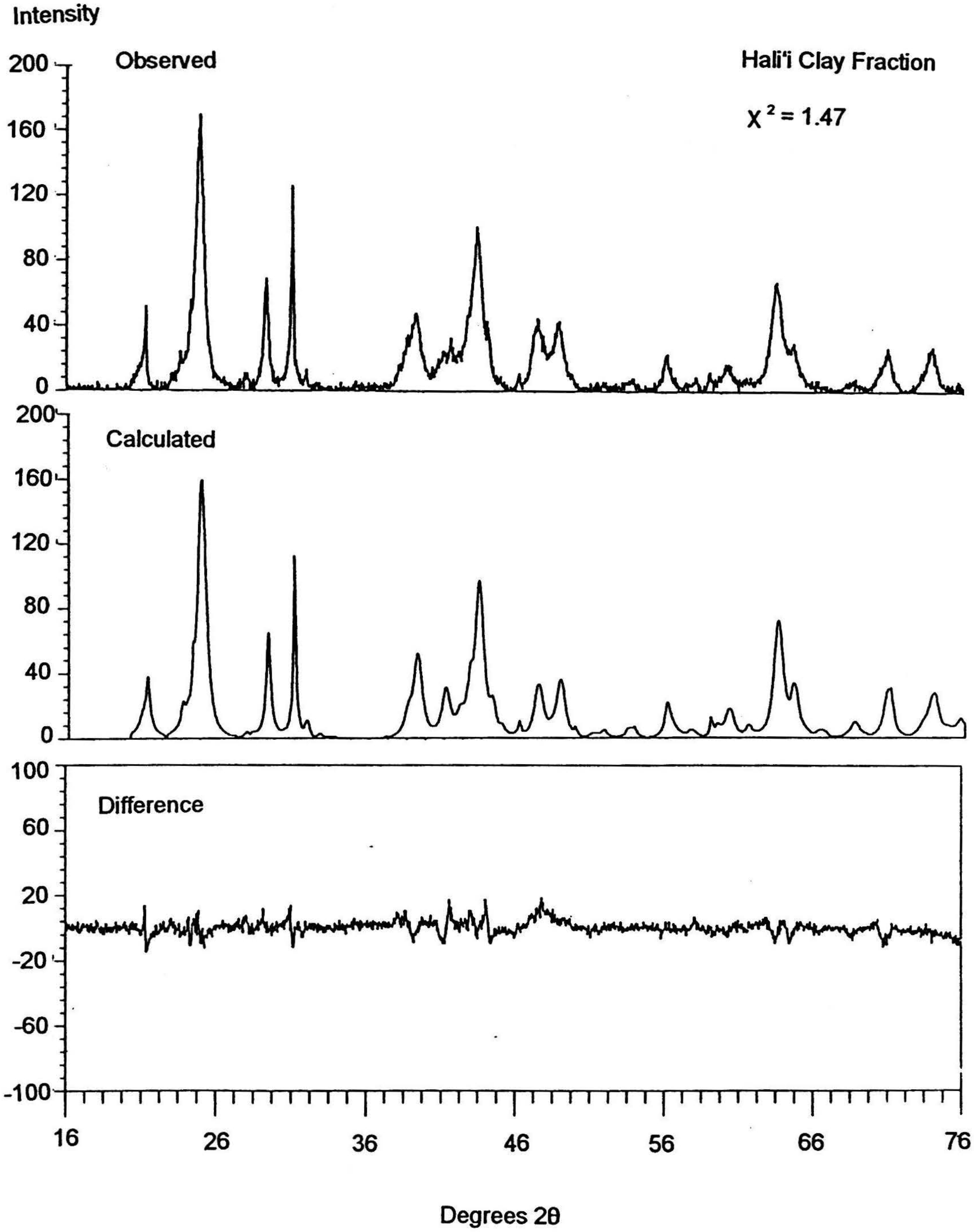


Figure 6. SIROQUANT© refinement of the XRD pattern for the Hali'i clay fraction.

The Hali'i clay fraction consists of gibbsite, hematite, goethite, anatase, rutile, and quartz. The contrast between the Hali'i clay fraction and the Waialua clay fraction are especially noticeable in the fitting of kaolinite peaks. Data for both patterns were collected with Co Kα.

Structure Factors

The integrity of the structure factors (an important factor in defining the intensity of each hkℓ peak) is dependent upon the type, number, and position of the atoms in the unit cell of each phase. Of utmost importance is the degree and type of ionic substitutions within the unit cell. Substitutions can usually be detected and compensated for by adjusting the unit cell dimensions to fit the peak positions on the observed XRD pattern. After unit cell dimensions or shape adjustments are made the atomic positions relative to the unit cell dimensions are changed, and hence the structure factors of the hkℓ peaks are altered. Fortunately, most unit cell dimension adjustments are minor and the relative changes in the structure factors are insignificant. There are cases, goethite for example, where the ionic substitutions are so extensive that relative intensities are severely altered. Unless the structure of substituted goethite is re-refined there is the danger that the abnormal peak intensities may be construed as a preferred orientation problem.

In such a case, a fit of the Rietveld pattern to the observed pattern will not be successful.

Preferred Orientation

If preferred orientation is moderate and the correct oriented hkℓ plane is recognized, then a successful compensation can be made. Problems result when a phase assumes a preferred orientation in two different hkℓ directions such as sometimes occurs with the phyllosilicates. Soils that contain approximately equal amounts of dehydrated halloysite and kaolinite have been observed to orient on the 00ℓ planes of kaolinite and the 110,020 planes of halloysite. In such a case an adequate correction for preferred orientation cannot be made because the current program treats the two minerals that produce a generic 7.2Å as a single mineral. A less than satisfactory compromise between the two orientation planes is the only action that can be taken in such a case.

Microabsorption

The SIROQUANT program has the facility to correct for microabsorption if the mean particle sizes of the different phases are known. If the clay fraction of a soil has been separated by centrifuge, presumably the largest particles in the sample will be 2µm. When all of the particles are approximately the same size, microabsorption differences due to differences in mass absorption can be corrected by the Brindley method (Brindley, 1945). The Brindley correction is based on X-ray path length in the particle as well as the mean mass absorption. Therefore, errors in microabsorption corrections occur when the particle sizes of the various phases differ considerably and are unknown.

Background Removal

The removal of background is subjective on the part of the program user. Experiments have shown that unless there are gross errors in the removal of background there are negligible differences in the outcomes of the analyses. The responsibility of the program user is to recognize the presence of trace phases. If trace phases are missed or ignored they are, in effect, removed from the observed pattern with the background and are not included in the total of the crystalline phases. Errors in such a case are small but none the less are accumulative if more than one trace phase is missed.

POSSIBLE ERRORS IN SAMPLE PREPARATION

Sample and Spike Weights

Sample preparation errors can appear during weighing and blending. Weighing errors can occur as a result of moisture factor differences between the sample and the spike. Unless both the sample and spike are dried at the same moisture levels, the exact percentage of the spike will be in error. Sample and spike drying require that both materials must be cooled for the same length of time and under the same humidity conditions so that absorbed moisture will be near the same for the sample and the spike. Normally the sample and spike are cooled in a desiccator to minimize the amount of moisture that is absorbed. The sample and spike are weighed to the nearest one-tenth of a milligram. Unless weighing is done in a "standard" amount of time the sample will gain weight while on the weighing pan. In an effort to minimize weight gain during weighing the moisture factor is determined by a "standardized" method (cooling and weighing times) and the samples are stored in a desiccator until they are blended with the spike.

Phyllosilicates

The phyllosilicates present a special problem because their hkℓ files are compiled on the basis of "perfect crystals." Soil phyllosilicates are normally very short-ranged and disordered. Their observed hkℓ peaks in no way resemble those of "perfect crystals." An attempt has been made to compensate for the differences between the Rietveld patterns and the observed patterns by editing the hkℓ files including the structure factors. Even with the edited hkℓ files the Rietveld fit to the observed pattern is a compromise. Thus, unavoidable errors in the determination of the phyllosilicates has its effect, large or small, on the estimation of the amorphous content of a soil.

Sample-Spike Blending

Blending presents a not particularly obvious problem. The clay fraction of a soil must be dried before weighing which results in aggregation. Ideally, both the sample and the spike should be close to 2µm in particle size. Actually the soil may consist of assorted sizes of relatively large aggregates, whereas the spike material may be close to 2µm in size. The blend of such a mixture is less than homogeneous. In order to minimize the inhomogeneity of the mixture the soil sample must be thoroughly ground in a mortar to ensure the smallest aggregate size as possible. The sample and spike must then be kneaded in a mortar until the mixture is as homogeneous as possible.

XRD Mount Preparation

The preparation of the mount provides another possibility for error due to a possible separation of the sample and the spike. Spike and sample segregation presents the greatest possibility if the particle sizes differ greatly. If the surface of the mount is trawled heavily the largest particles are likely to migrate to the surface and the fine material will settle into the body of the sample. Sample surface trawling should, therefore, be minimized for reasons of size separations and the exacerbation of preferred orientation.

CONCLUSIONS

The objective of this research was to devise a methodology for the estimation of the crystalline and amorphous fraction of the clay fraction of soils using the Rietveld method. Another objective was to estimate the oxide composition of the Rietveld calculated amorphous material by subtracting the crystalline oxide composition (as determined by the Rietveld method) from the total oxide composition (as determined by XRF). The difference in oxide composition of the oxalate extractable portion and the Rietveld amorphous material of the clay faction was also performed.

In terms of methodology the following is a list of some suggestions for preparing soil samples for Rietveld analysis:

1) The amount of spike necessary for amorphous content determination is related to the amount of amorphous material present in the sample. For example the average amount of amorphous material present in Hawaiian soils was 50%. When 50% amorphous material is present the optimum amount of spike needed for amorphous content determination is 30%.

2) Blending of the sample and spike should be done in a mortar and pestle using a kneading motion.

This is done to ensure that no additional amorphous material is created during sample preparation and to ensure that the samples are homogeneous.

3) Corundum SRM 676 was chosen over silicon SRM 640a as a spike because corundum has less of a dilution effect at the 30% spike level and also because corundum displays more hkℓ peaks than silicon.

4) Corundum SRM 676 was oriented on the 104 plane for all amorphous content determinations.

5) The sample and the spike should be approximately the same size. The average size of both the sample and spike should be less than <24μm. This is done to both minimize microabsorption and to achieve a "powder average."

6) A 10 second per step integration time afforded the best ESD and allowed trace mineral amounts to be easily detected on the XRD pattern.

7) No significant difference in Rietveld calculated percentages was detected among samples with or without H_2O_2 treatment.

The large disparity between the total amorphous material as estimated by the Rietveld method and oxalate extractable amorphous material can be explained on the basis that the two methods account for different portions of the clay fraction. The amorphous material that is removed by oxalate extraction has been traditionally referred to as the "active" portion of the soil.

The total amorphous material is composed of both the chemically extracted gels and the vitreous materials that are not easily removed by chemical extraction methods. Vitreous particles are apparently resistant to chemical attack as are the crystalline particles by, for example, acid ammonium oxalate.

In terms of importance, oxalate extractable amorphous material may correlate better with phosphate and other anion sorption than the total amorphous fraction. Caution must be taken when assigning the significance of anion sorption to the total amorphous fraction of a soil as found by the Rietveld method.

An outstanding asset of the determination of the total amorphous fraction of a soil is that, for the first time, the correct crystalline mineral percentages can be found. A reliable estimate of the total amorphous material may have profound consequences for soil classification. Soils thought to be highly crystalline on the basis of 5% oxalate extractable material may be found to contain >50% total amorphous material such as is the case for the Makapili soil. For some soils the total amorphous fraction may be much more important than the dominant crystalline mineralogy for classification purposes at the family level, Only the clay fraction can be analyzed by X-ray diffraction to achieve a "powder average" so that all $hk\ell$ planes are equally represented and to minimize microabsorption. Any amorphous material in the silt and sand fractions are, therefore, not included in the total amorphous fraction. There is a possibility that if the silt and sand fractions are ground to clay size, amorphous material may be produced. Future research is needed to determine how to analyze the silt and sand fractions and what the possible significance of the amorphous material in these fractions would be.

APPENDIX A

DEFINITIONS

Amorphous Material: a) Any substance that does not produce recognizable crystalline phase peaks on the observed XRD pattern. b) Any contribution to the observed pattern that can be fit by a Rietveld polynomial and removed.

Background: Those intensities on an observed XRD pattern that cannot be recognized as contributing to a crystalline phase. Unfortunately, identifying and removing background from the observed XRD pattern is, for the most part, a subjective procedure. There is always the possibility that trace crystalline phases might not be recognized and removed with the background and thus treated as amorphous.

Crystalline Phase(s), Component(s): Any substance(s) that produces recognizable peak(s) on the observed XRD pattern. "Recognizable peaks" does not necessarily imply that the observed pattern can be adequately fit by the Rietveld pattern. In the case of disordered phyllosilicates the fit by the Rietveld pattern may be less than ideal, but the crystalline component(s) is/are recognizable and is/are not included in and removed from the observed pattern with the background.

Crystallite: A three-dimensional array of unit cells that define a unique crystalline material that is small, usually <2μm equivalent spherical diameter, and is often a constituent of a particle.

Domain Size: a) The extent to which unit cells repeat in three dimensions within a crystal lattice until a plane defect is encountered. b) In the case of phyllosilicates the repeat distance is expressed in terms of numbers of basal planes in two dimensions before a plane defect is encountered.

Extinction: (Primary extinction) A result of the destructive interference of multiple reflections within a diffracting crystal which results in a reduction in the diffraction intensity that is directly proportional to the domain size. "Perfect" crystals having large domain sizes exhibit more extinction, less diffraction intensity, than "imperfect" crystals having small domain sizes. Very small or "imperfect" crystals, therefore, may exhibit little or no extinction.

Particle: a) A composite consisting of crystallites and amorphous materials. b) A small, usually <2μm aggregate.

Preferred Orientation: Minerals having plate-like or needle-like morphologies tend to become aligned with the surface of the XRD sample during preparation, a condition referred to as preferred orientation. Under conditions of preferred orientation the intensities of certain hkℓ peaks on the XRD observed pattern will be higher than the powder average of the remaining peaks. Without a correction for preferred orientation the Rietveld pattern cannot be fit to the observed XRD pattern.

Spike: A crystalline phase that is added to the sample in a precise amount that serves as an internal standard.

Rietveld Spike: Weight fraction of an internal standard that is reported by the Rietveld program. If amorphous material is present the value of the Rietveld spike will be greater than the value of the added spike. In the absence of amorphous material the Rietveld spike will be equal to the added spike. The Rietveld spike can never be less than the added spike.

Observed XRD Pattern: An accumulation of experimentally obtained X-ray diffraction (XRD) intensities that span a definite range of Bragg angles.

Rietveld Pattern: A computed XRD pattern that is produced by using *ab inito* principles of X-ray diffraction.

Pattern Fitting: A superposition of a Rietveld pattern over an observed XRD pattern. In cases of good crystallinity the superposition of the two patterns may be nearly perfect. In cases of poor crystallinity, such as the disordered phyllosilicates, the superposition of the two patterns may be a "best fit" compromise. A low Chi-square value may be misleading. The best indication of convergence or near convergence is conveyed by the superposition of the two patterns.

APPENDIX B

FIGURES

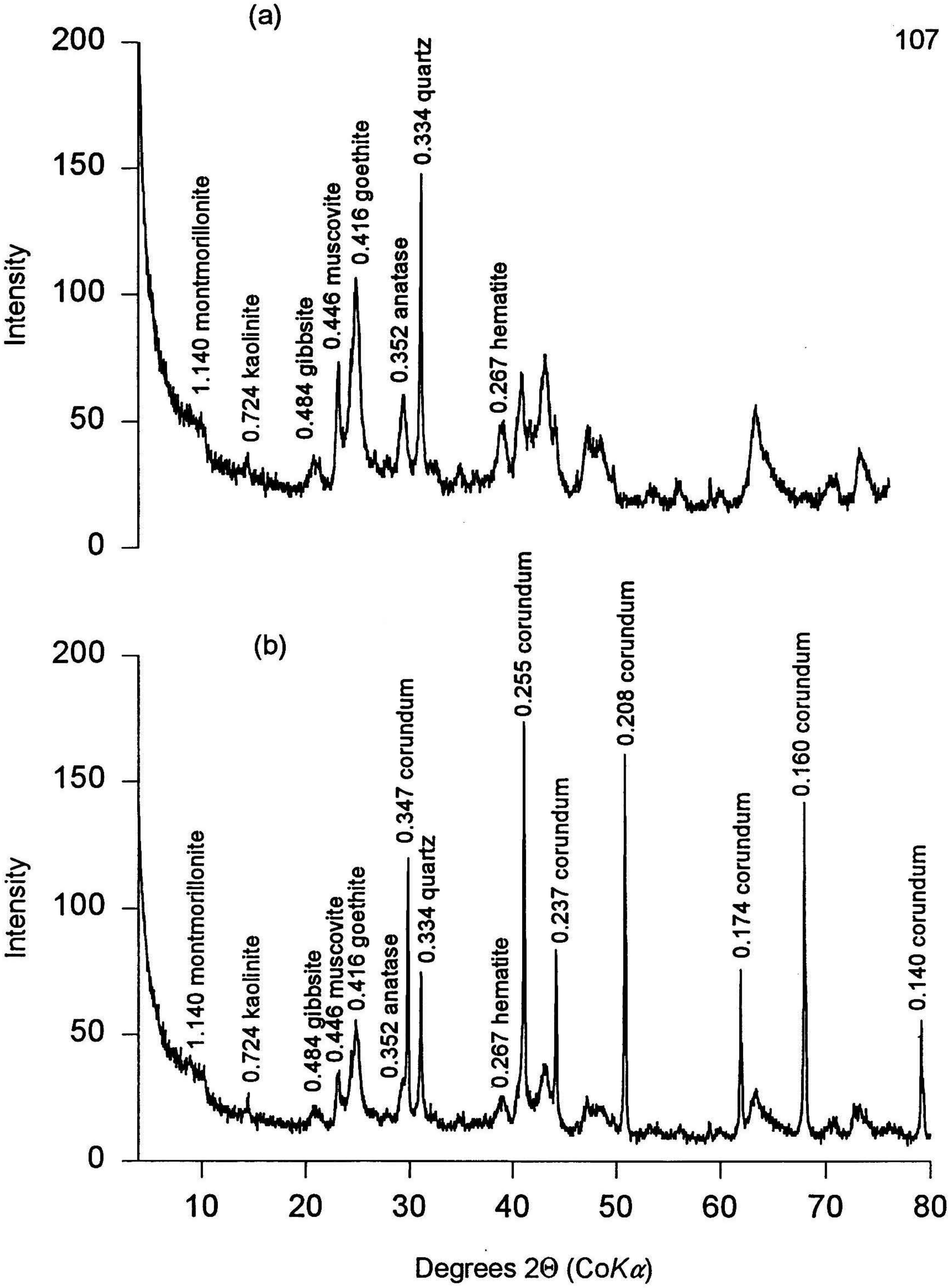


Figure 7. Ha'iku clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

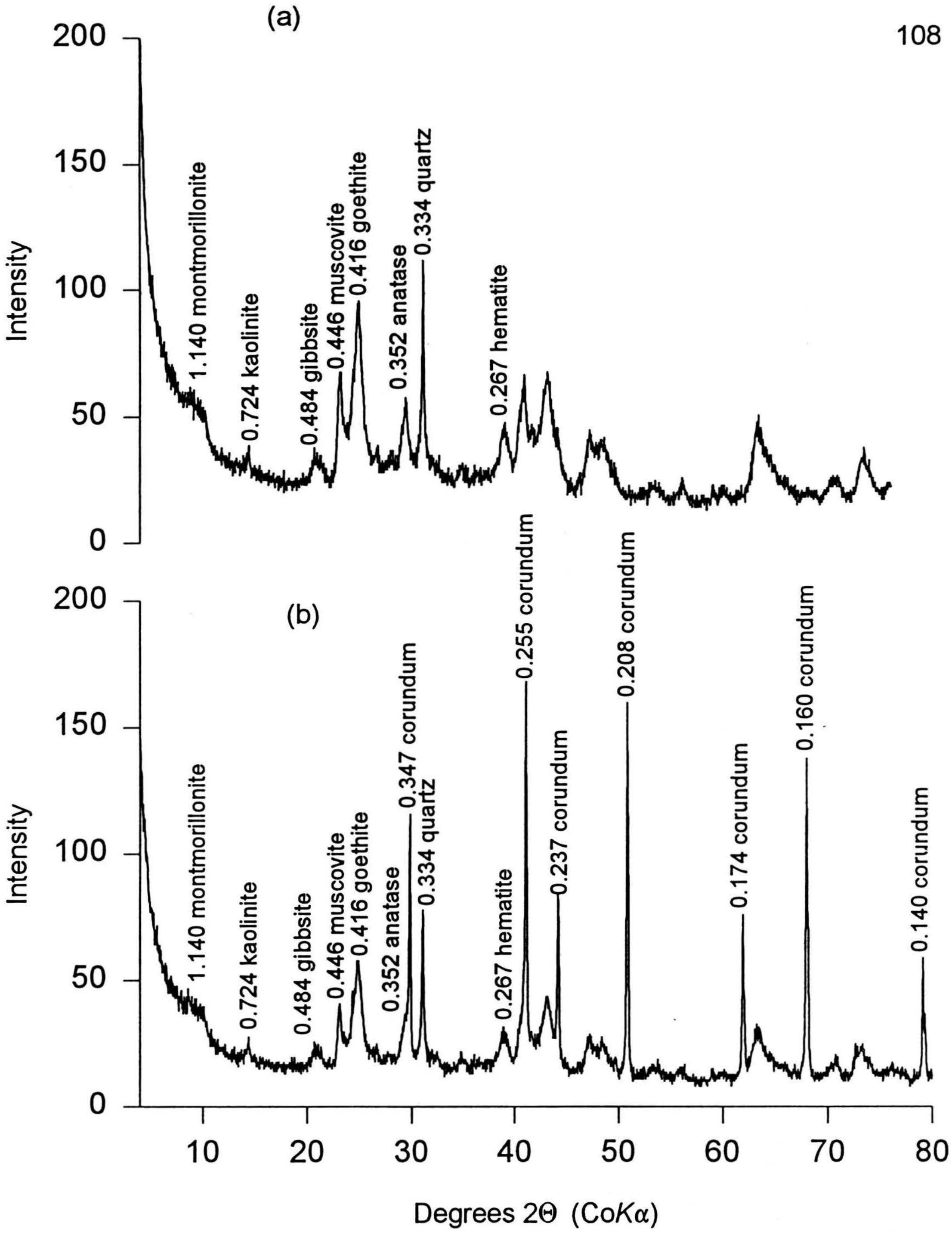


Figure 8. Ha'iku clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

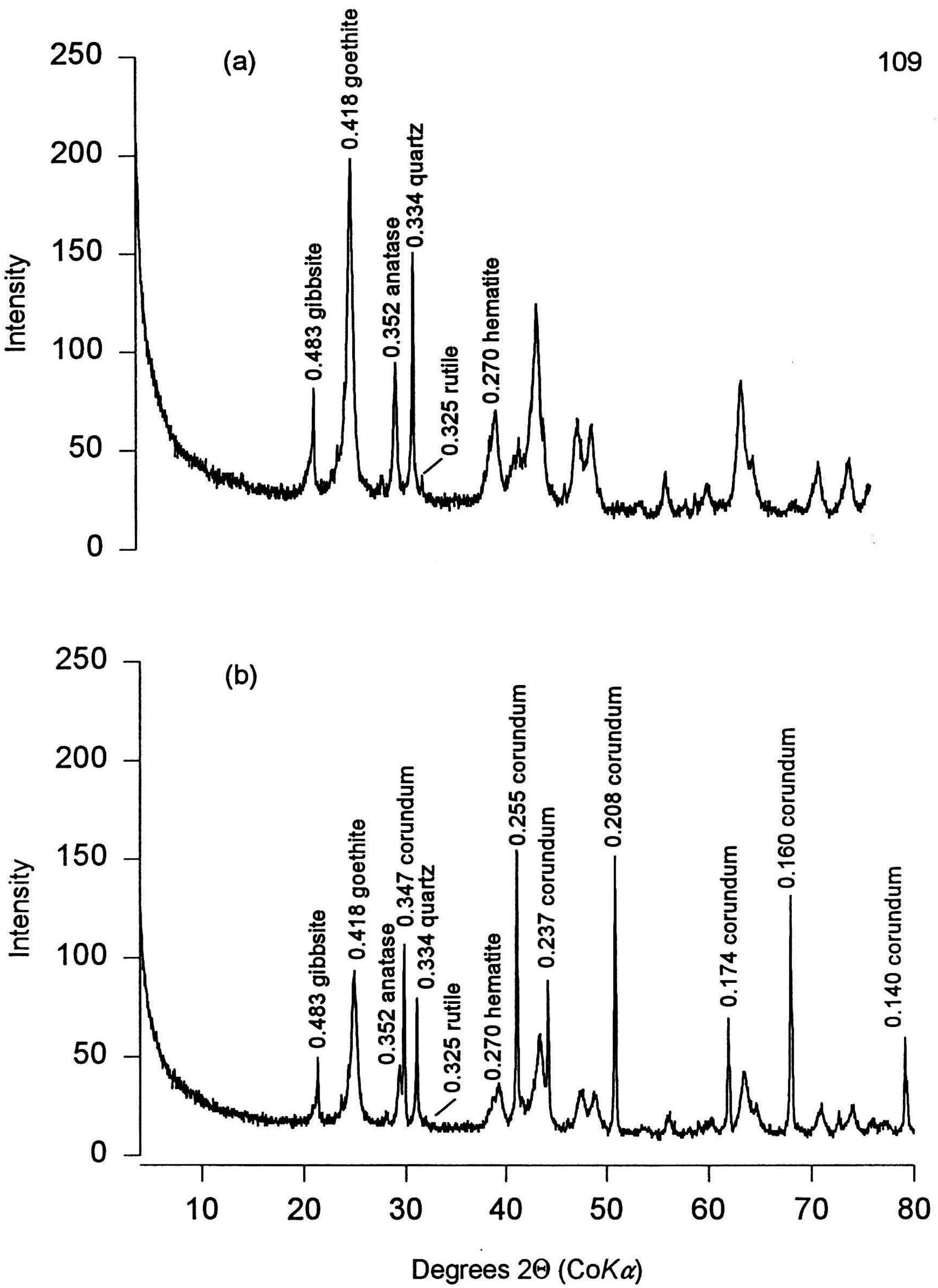


Figure 9. Hali‘i clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

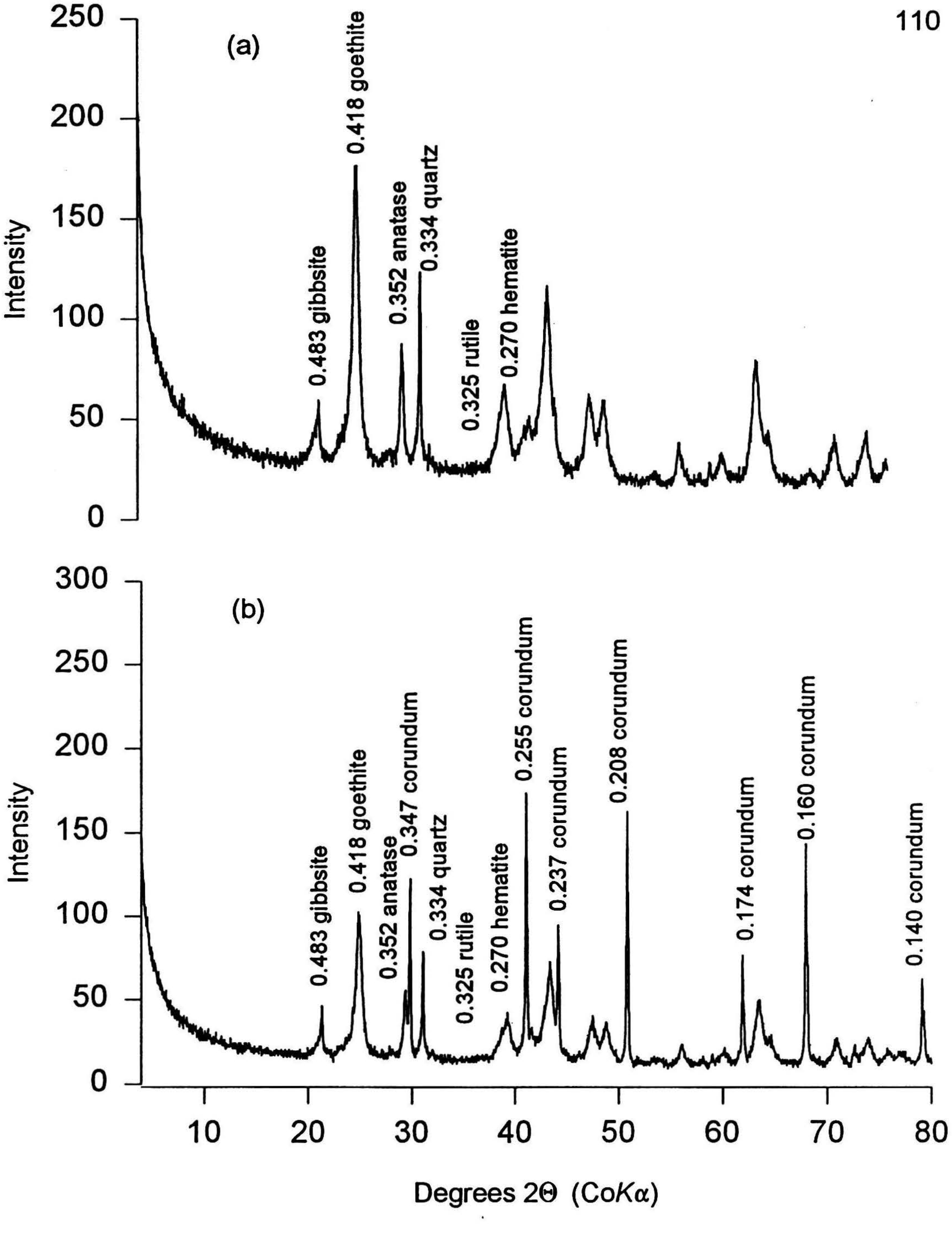


Figure 10. Hali'i clay with H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

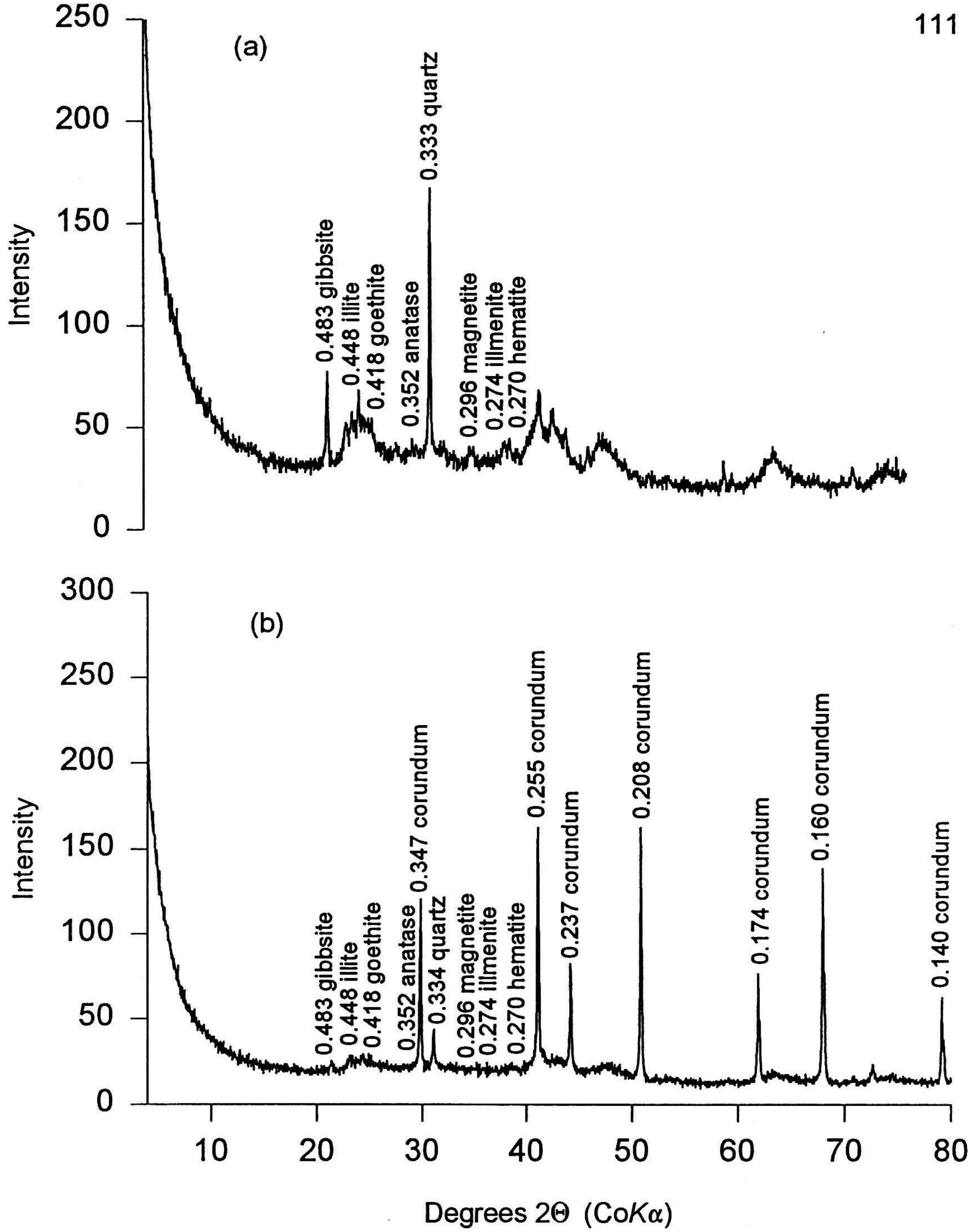


Figure 11. Kaiwiki clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

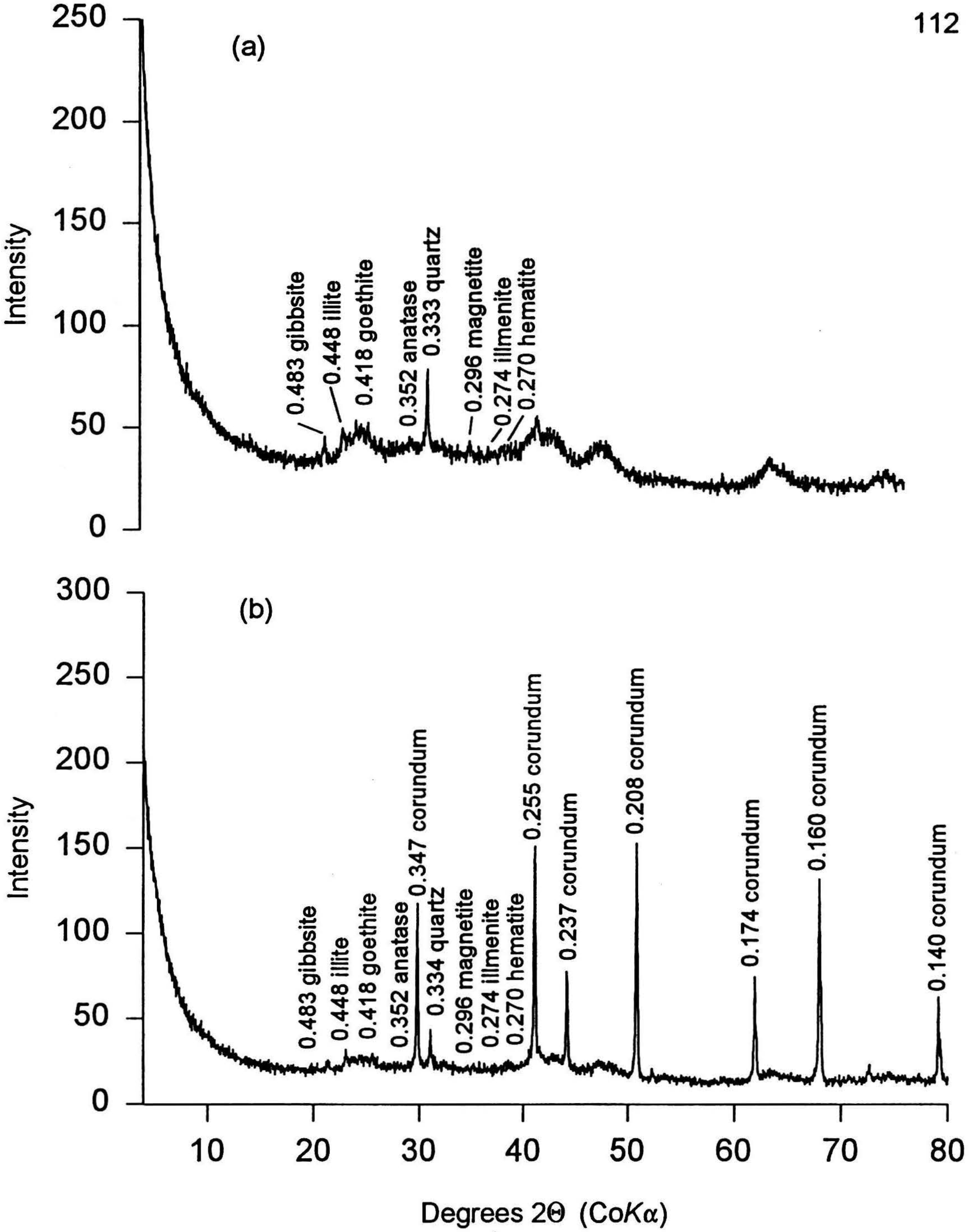


Figure 12. Kaiwiki clay with H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

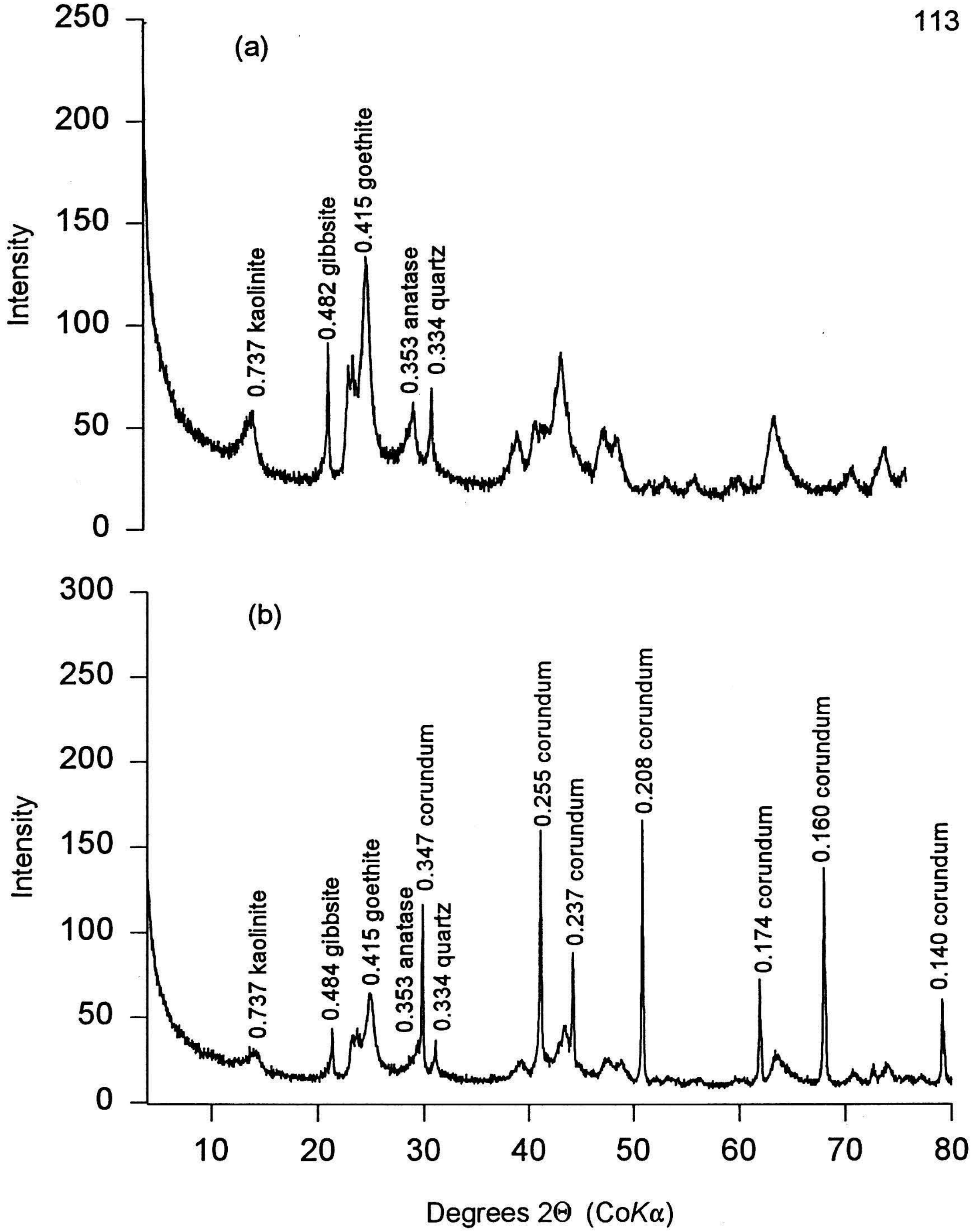


Figure 13. Kapaʻa clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

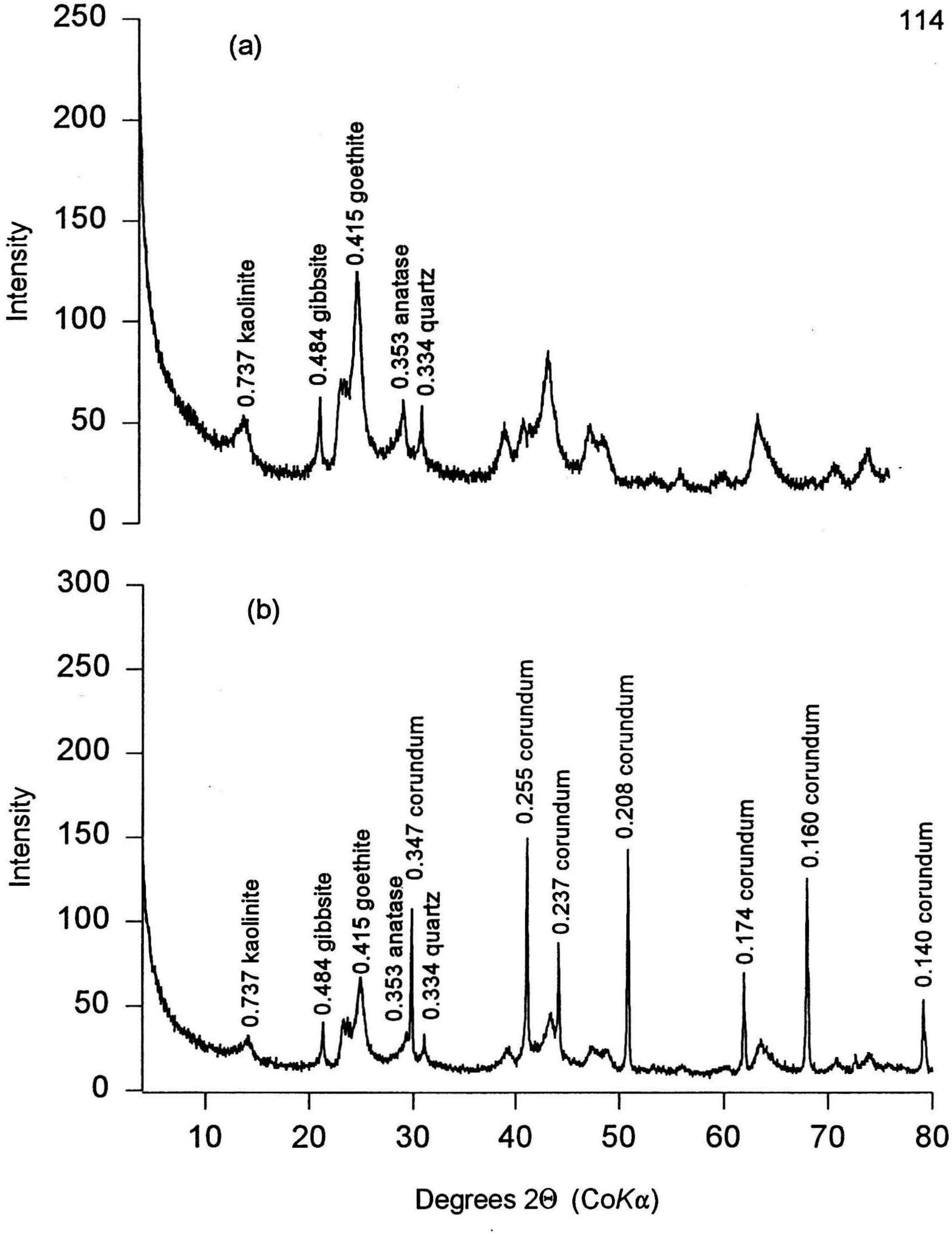


Figure 14. Kapa'a clay with H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

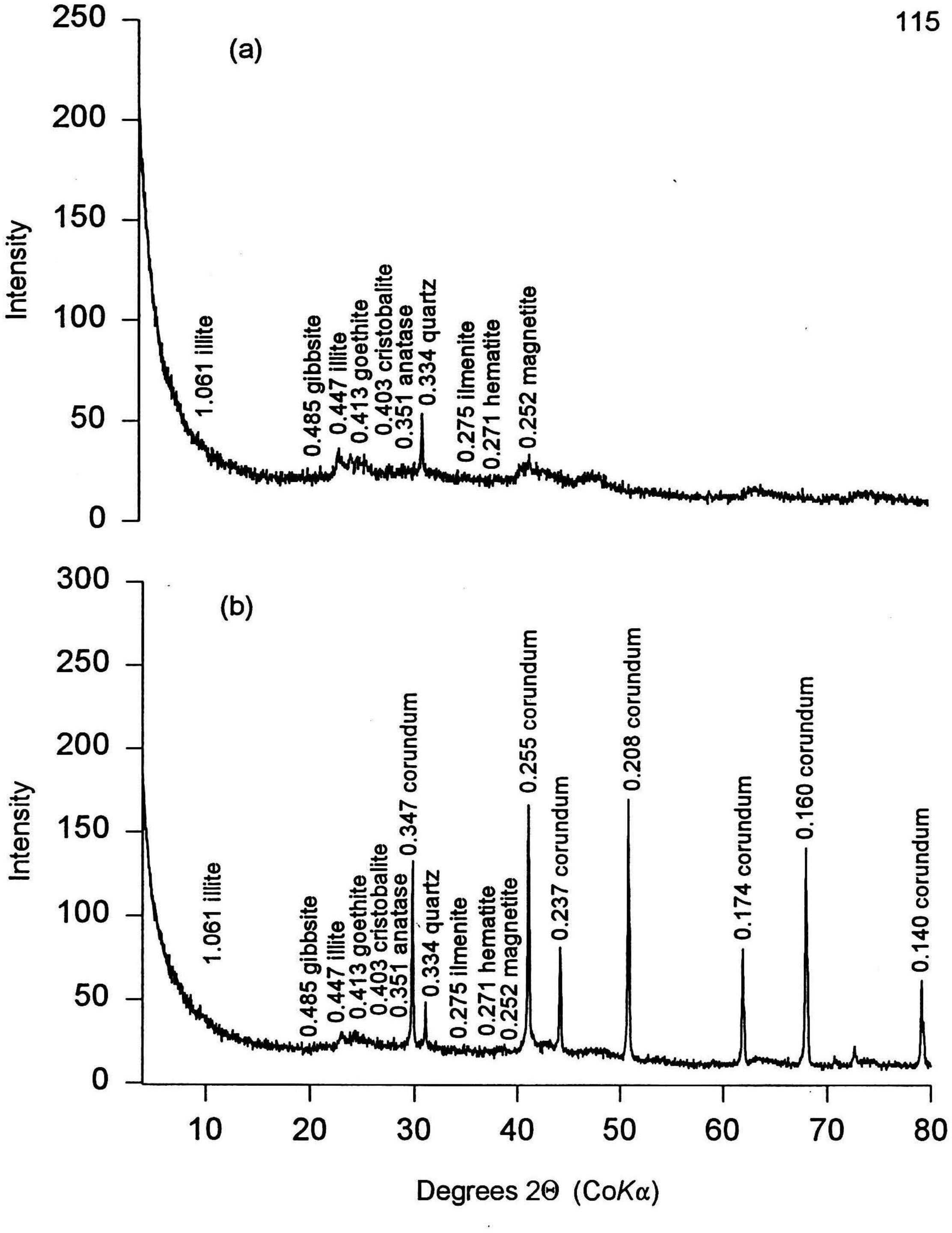


Figure 15. Maile clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

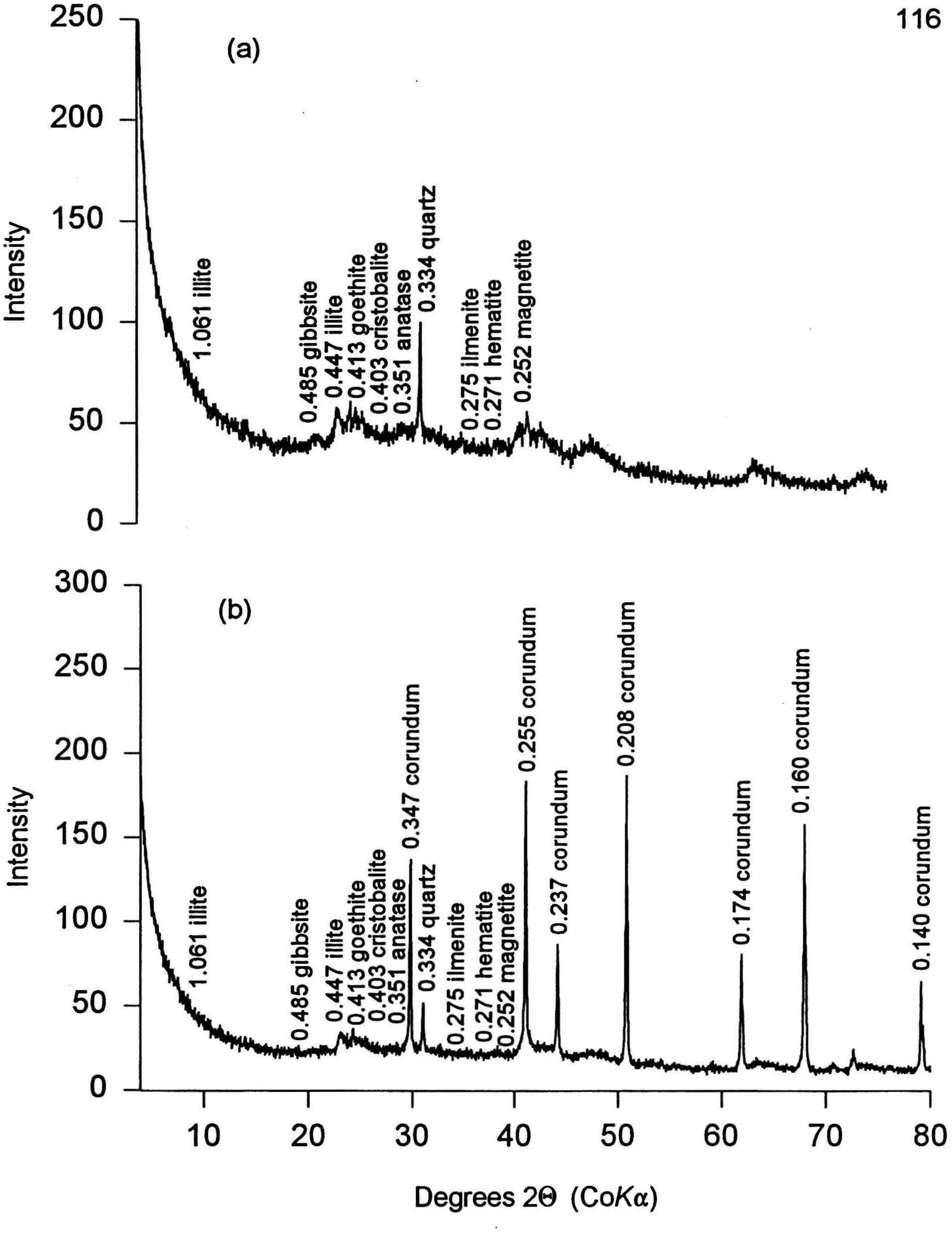


Figure 16. Maile clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

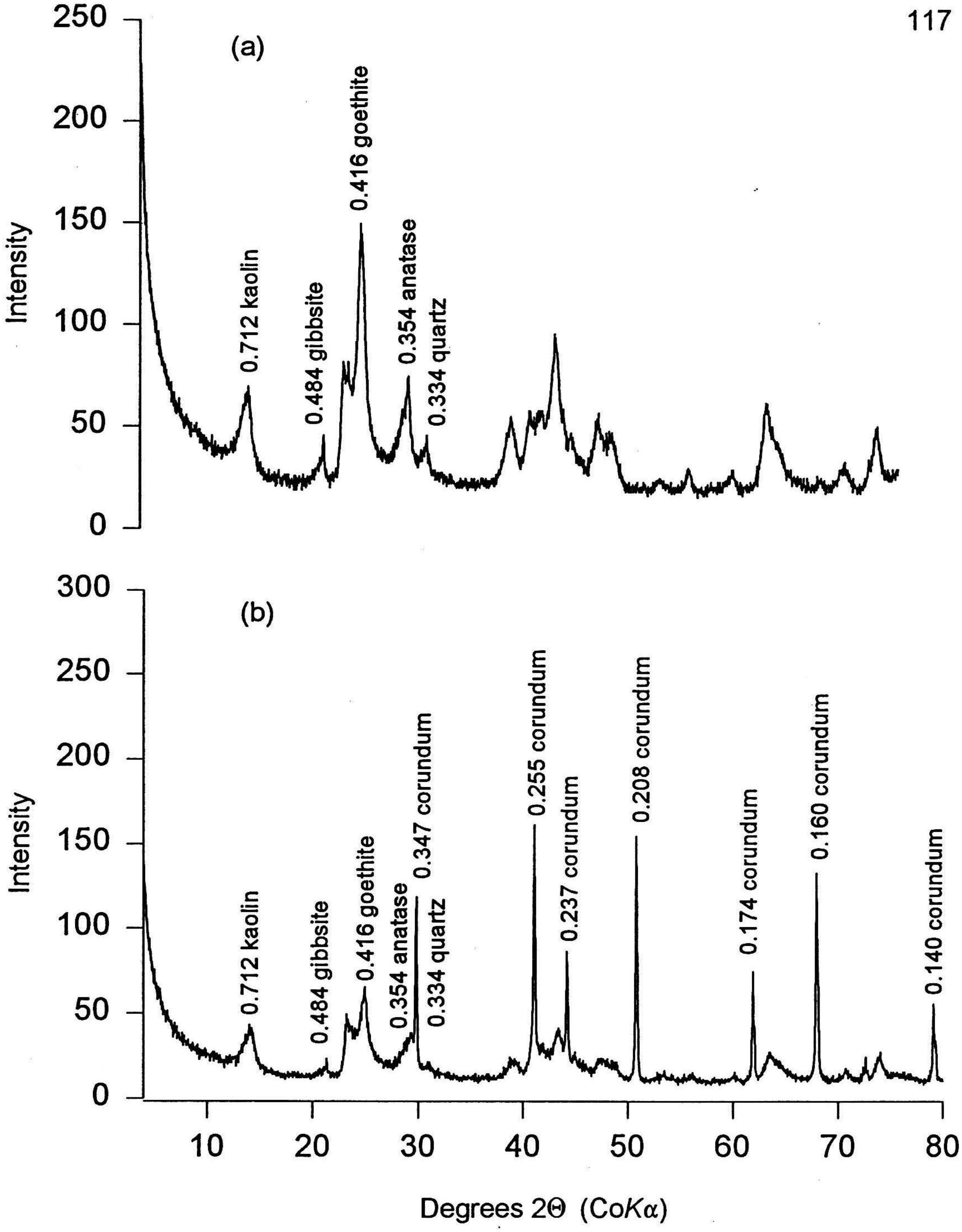


Figure 17. Makapili clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

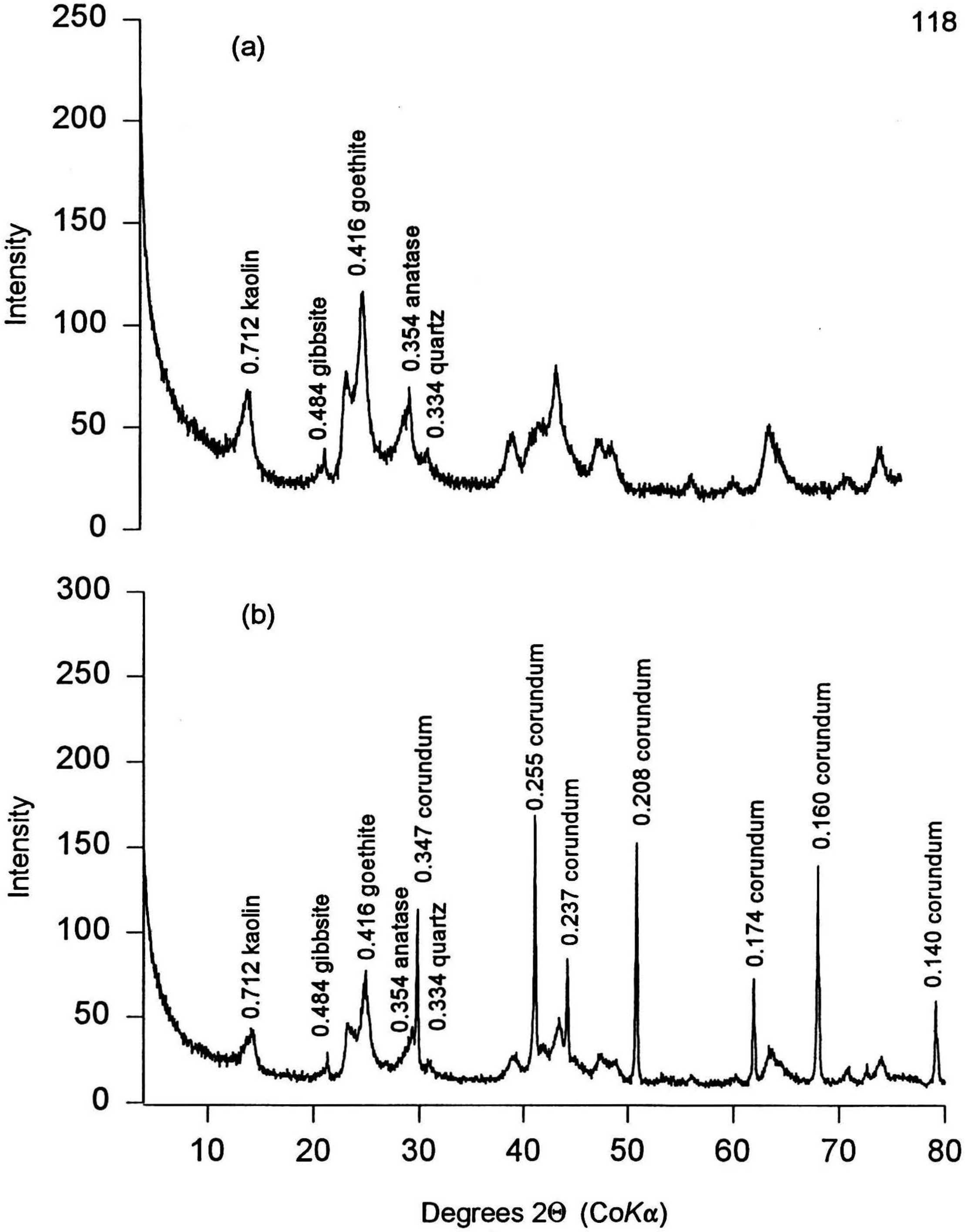


Figure 18. Makapili clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

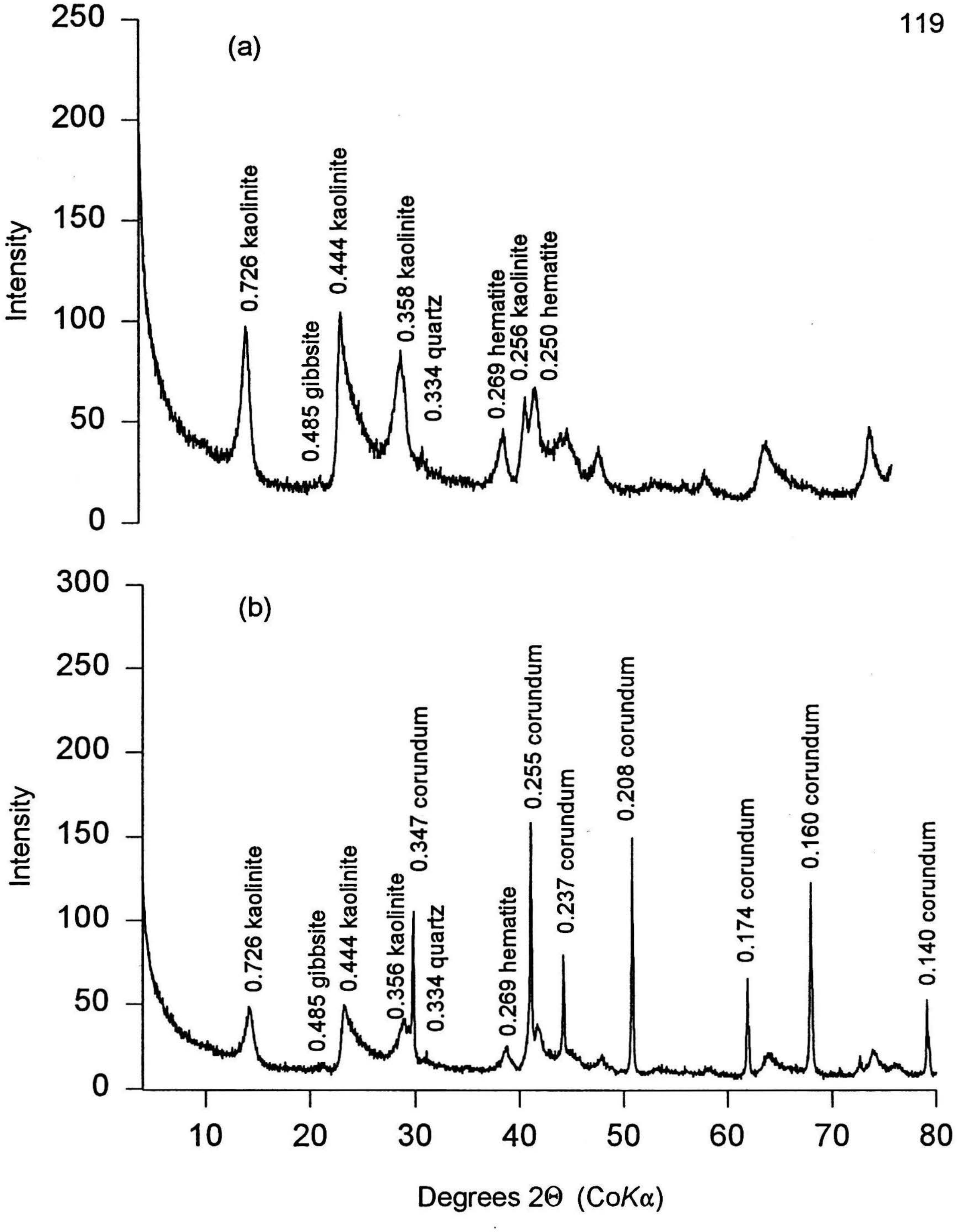


Figure 19. Moloka'i clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

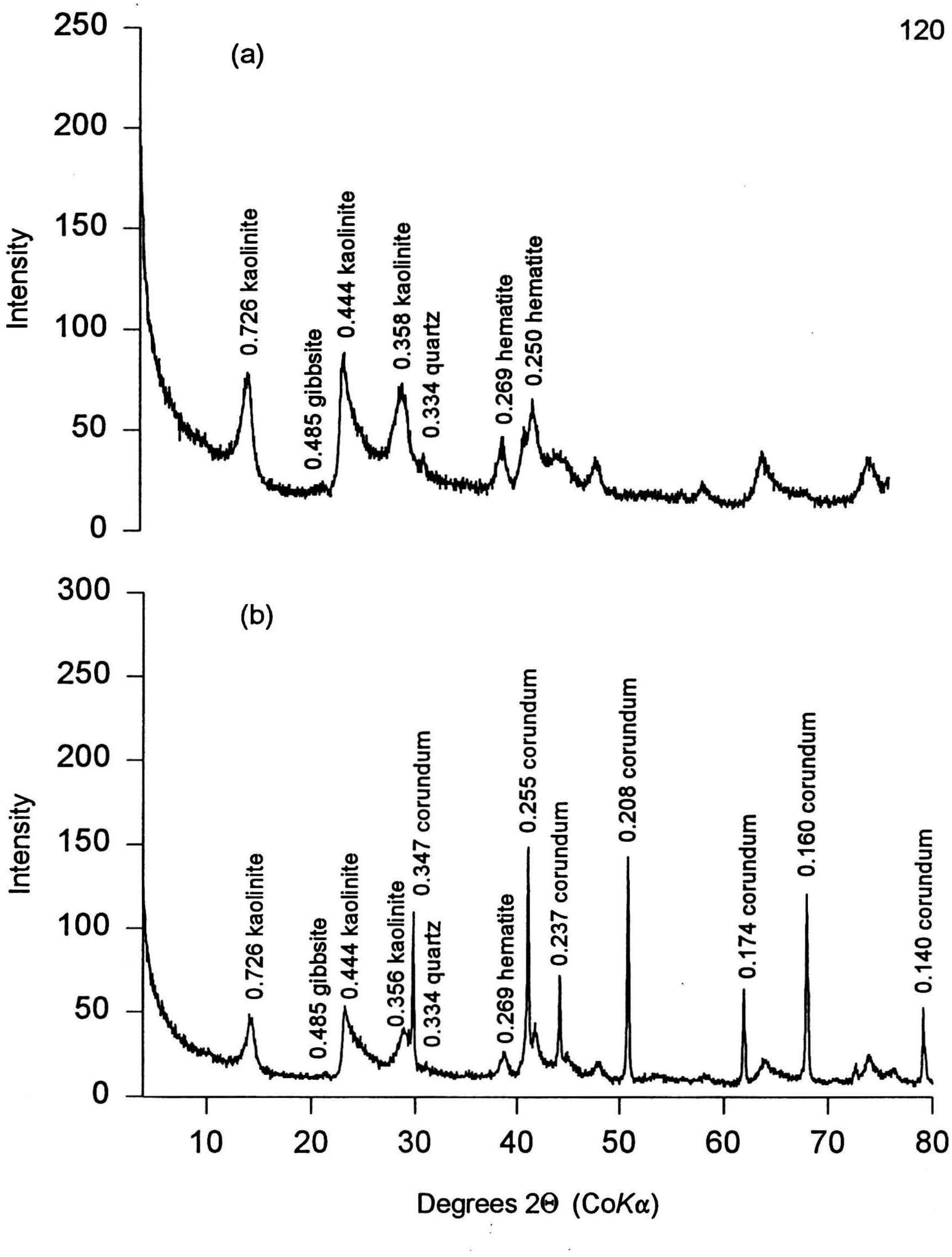


Figure 20. Moloka`i clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

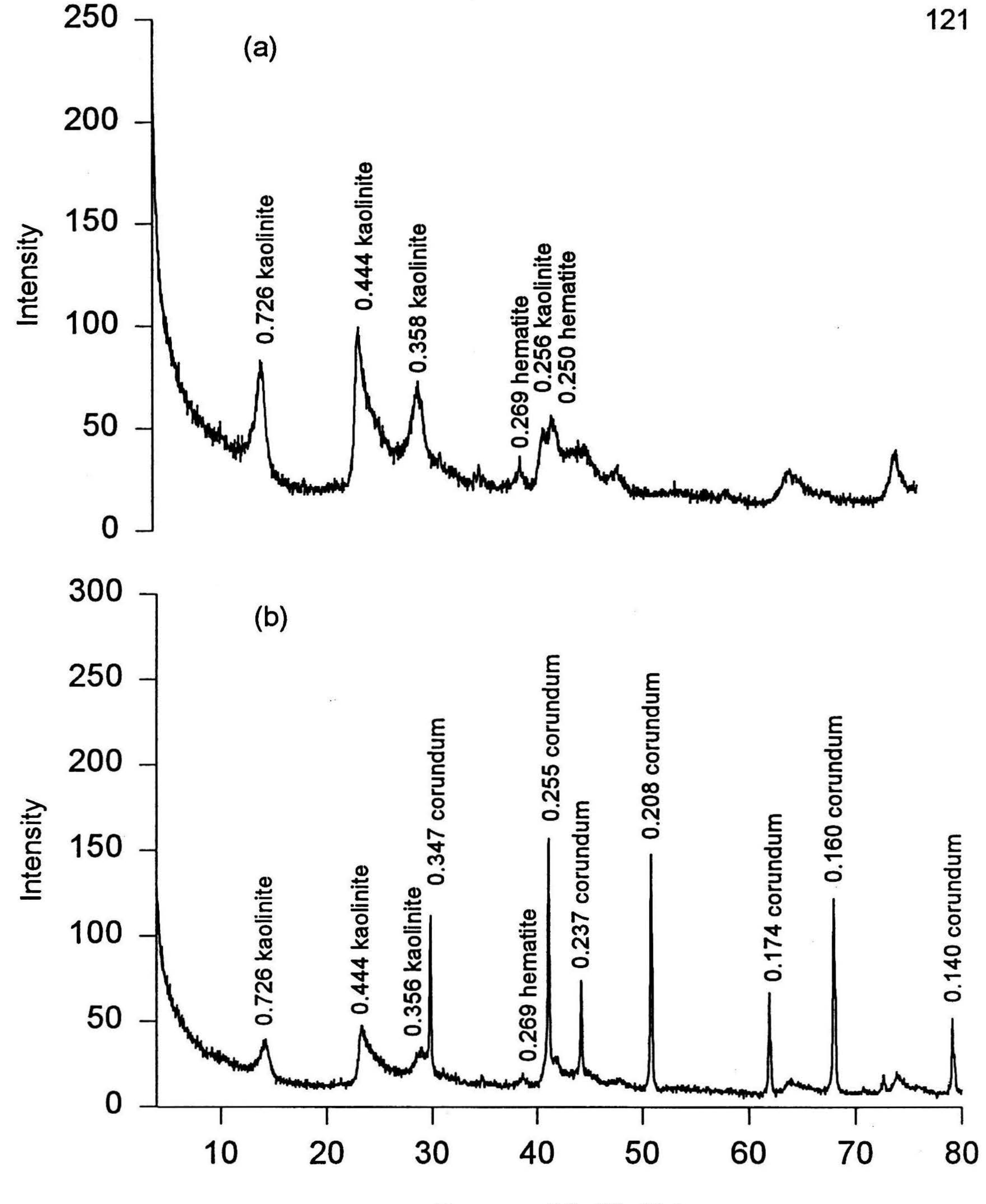


Figure 21. Pulehu clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

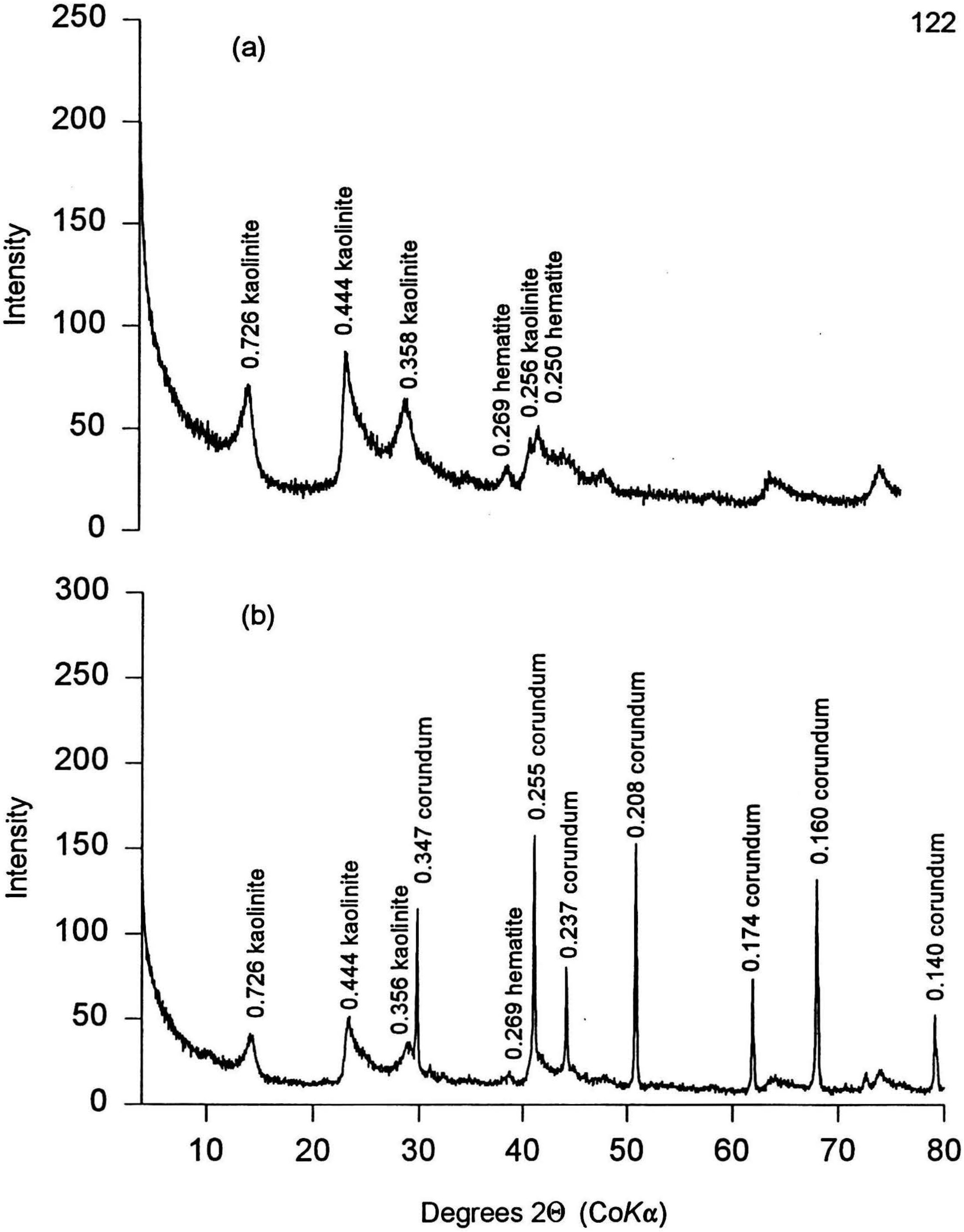


Figure 22. Pulehu clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

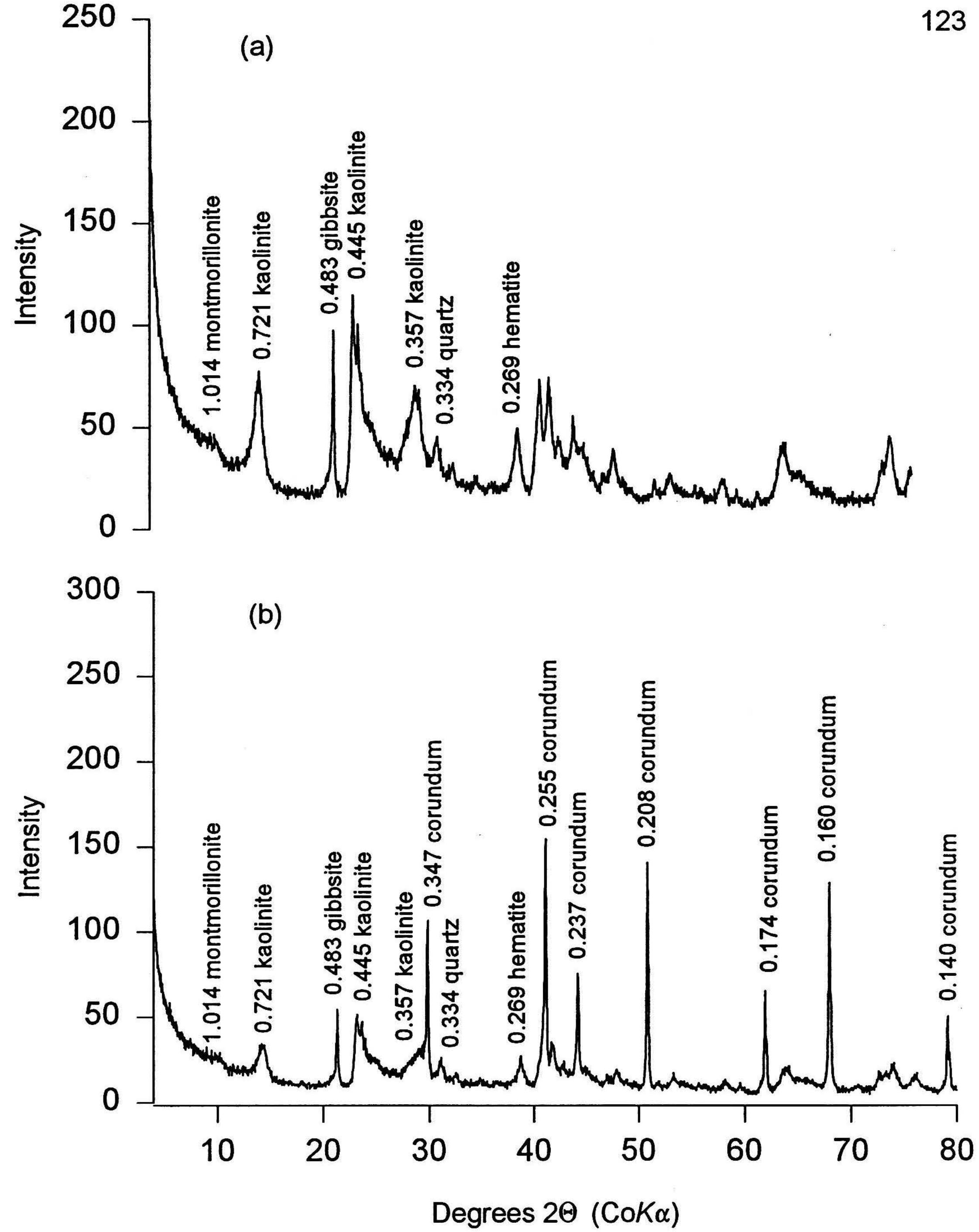


Figure 23. Wahiawa clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

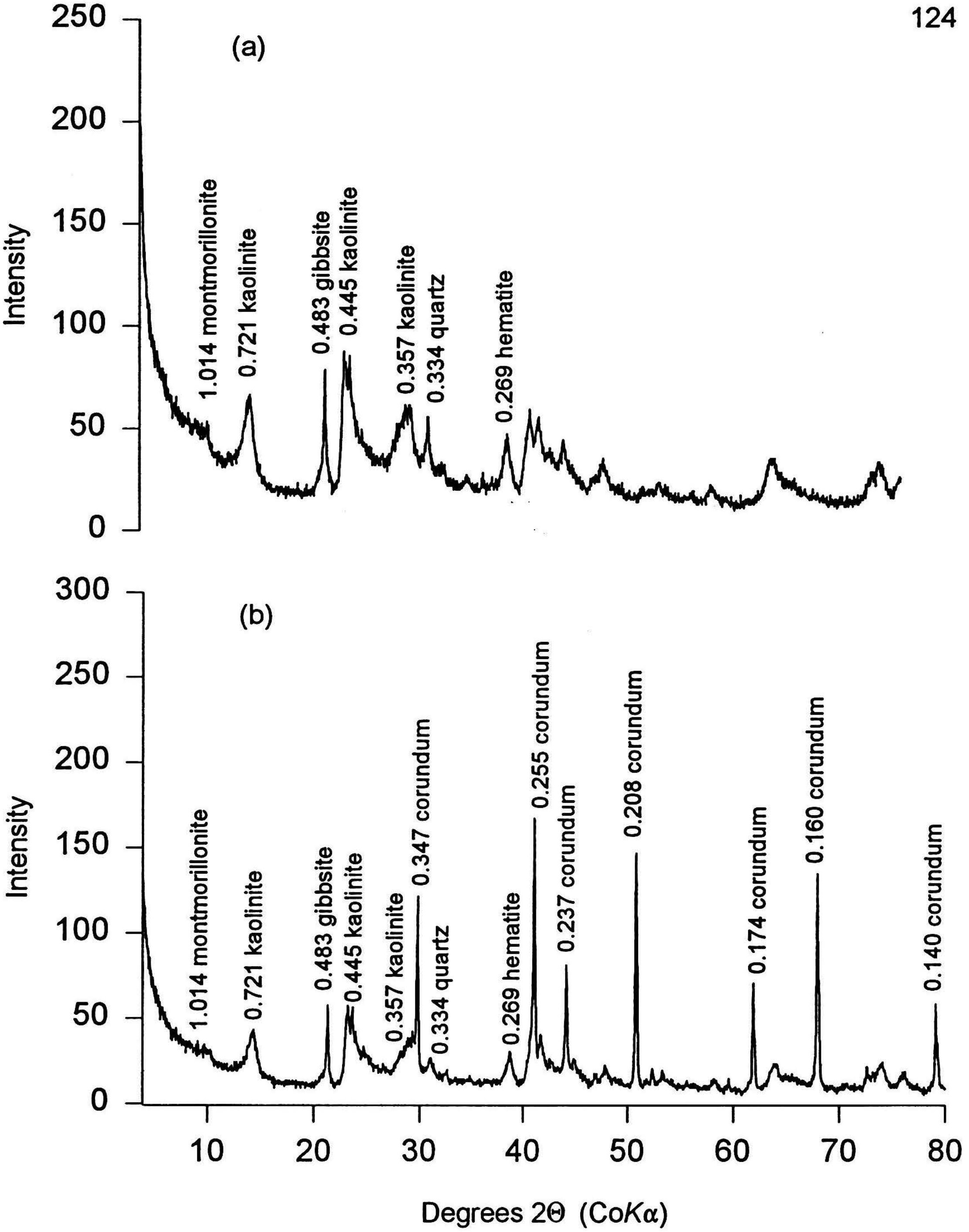


Figure 24. Wahiawa clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

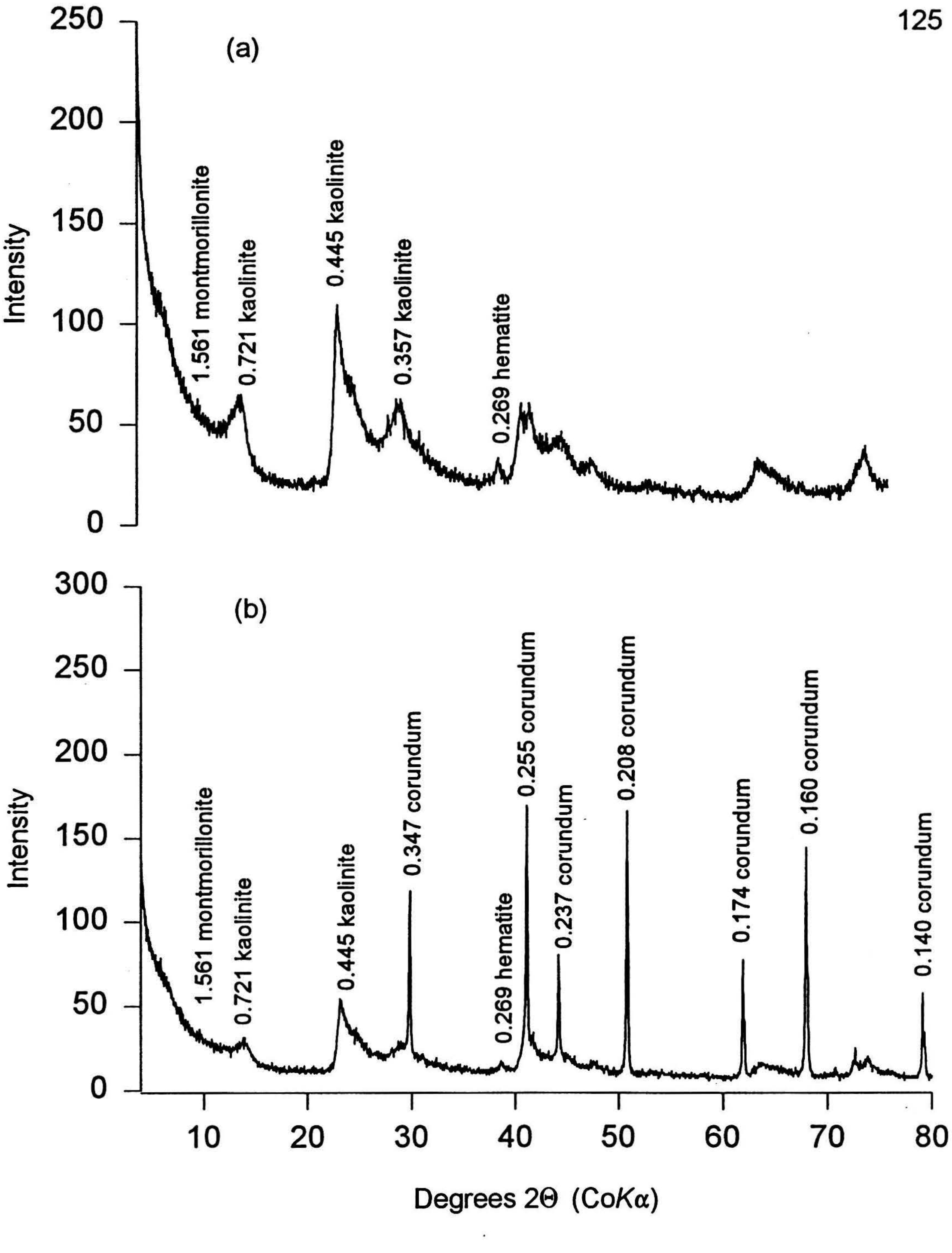


Figure 25. Waialua clay without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

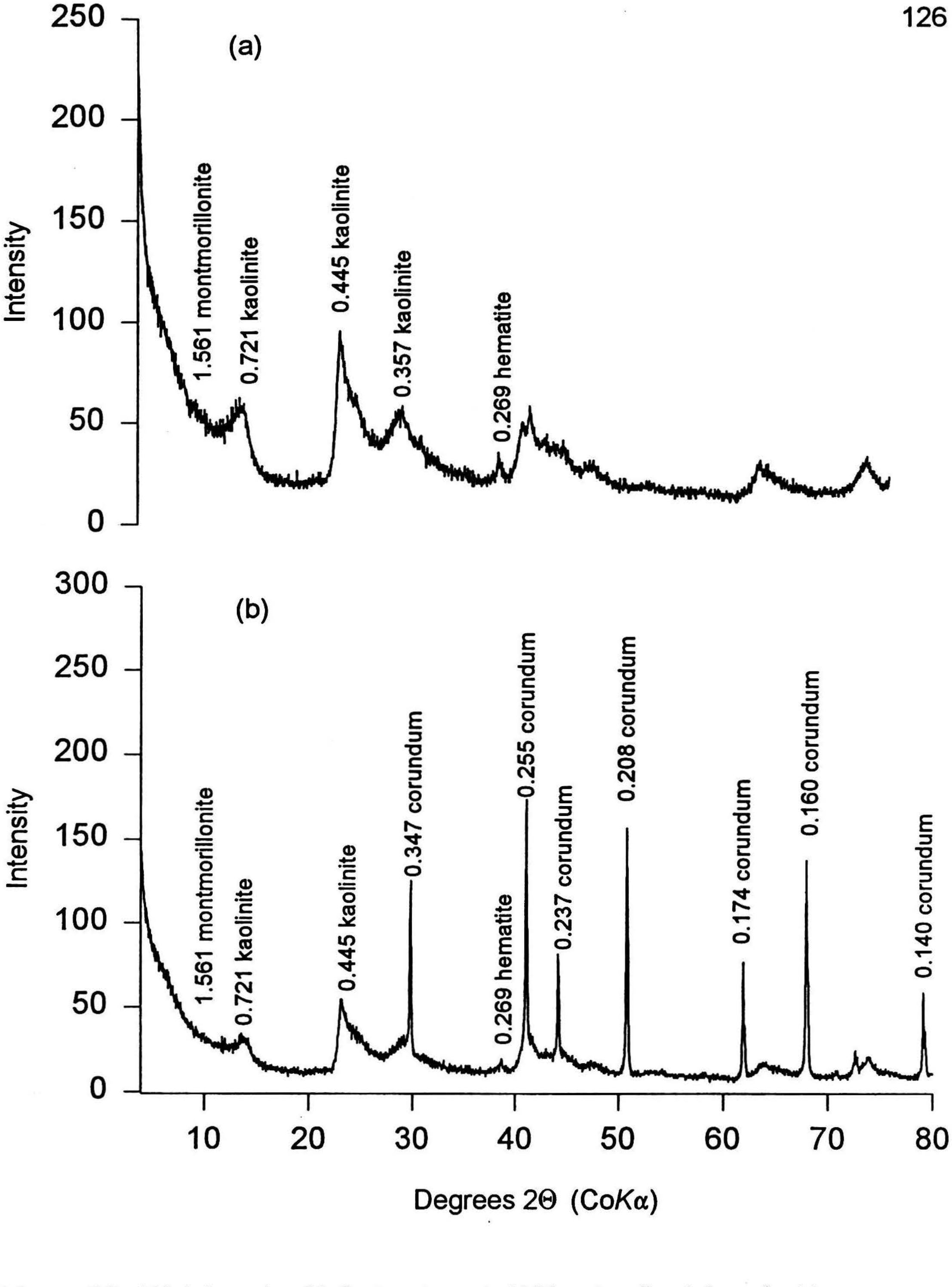


Figure 26. Waialua clay H_2O_2 treatment. Without spike (a) and with 30% corundum spike (b), (d spacing reported in nanometers).

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